RECYCLING OF WASTE COTTON TEXTILE CONTAINING ELASTANE FIBERS THROUGH DISSOLUTION AND HOT-PRESSING

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ABSTRACT

In the past ages, the textile industry has become one of the biggest industries. As the demand for textiles has grown, the concerns about the environmental impact of textile production and textile waste treatment have also grown. Cotton is one of the most common materials for textiles with good moisture absorbency and heat isolation but poor elasticity and wrinkle resistance. Therefore, elastic synthetic polymeric fibers such as elastane, are commonly mixed with cotton fibers for optimum garment properties. In this study, the recycling of waste cotton textiles containing elastane fibers into biodegradable packaging materials through dissolution and hot-pressing was investigated, and regenerated cellulose (RC) composite films with high tensile strength and water vapor barrier property were developed. In Chapter 2, the recent research on textile waste recycling and textile wastes-derived functional materials were reviewed, which mainly focused on the following three aspects: (1) textile waste management and textile materials, (2) recycling methods for textile waste, and (3) applications of recycled textile waste on the textile industry, environmental treatment, electrochemistry, engineering solutions, packaging materials, and micro-/nano-cellulose extraction. In Chapter 3, the dissolution and regeneration of waste cotton-elastane fabrics in H_2SO_4 aqueous solution, NaOH/urea aqueous solution, and LiCl/DMAc solution was performed. All three solvent systems could effectively dissolve the cellulose fibers while resulting in different forms of elastane components. The elastane fibers were unable to dissolve in NaOH/urea solvents but were partially dissolved in H_2SO_4 and completely dissolved in LiCl/DMAc solvent. The films produced from LiCl/DMAc solvent system obtained the best transparency, tensile strength, and water vapor barrier property contributed by the complete dissolution of elastane fibers. In Chapter 4, hot-pressing was used for RC composite films prepared with three solvent systems with different pressure and temperature. The RC composite films were hot-pressed at 120 °C/180 ℃ and 4.45 MPa/44.5 MPa for 15 min. The results revealed that the tensile strength and young’s modulus increased with the increase of hot-pressing temperature, while not affected by the increase of hot-pressing pressure. The water vapor barrier property of regenerated cellulose films could also be improved but further enhancement at elevated hot-pressing temperature was only found in films prepared by NaOH/urea system. In addition, the RC composite films prepared from LiCl/DMAc system hot-pressed under 180 ℃ and 4.45 MPa showed the highest tensile strength (202.10 ± 6.82 MPa), Young’s modulus (12.79 ± 1.11 GPa), and lowest WVP ($2.89 \pm 0.37 \times 10^{-9}$ g m^{-1} h^{-1} Pa^{-1}). Overall, this research demonstrated that the waste cotton-elastane fabrics can be recycled and hot-pressing into RC composite films, which have potential applications as packaging materials. It also provides a promising strategy to relieve the environmental pressure caused by waste textiles.

RÉSUMÉ

Pendant les années passés, l'industrie textile est devenue l’une des plus grandes industries. L'augmentation de la demande de textiles s'accompagne de préoccupations croissantes concernant l'impact environnemental de la production et du traitement des déchets textiles. La fibre de coton est l'un des matériaux textiles les plus communs. Elle possède une bonne capacité d'absorption de l'humidité et d'isolation thermique, mais une faible élasticité et résistance au froissement. Par conséquent, les fibres polymères synthétiques, comme l'élasthanne, sont couramment mélangées aux fibres de coton pour optimiser les propriétés des vêtements. Dans cette étude, le recyclage des déchets textiles en coton contenant des fibres d'élasthanne en matériaux d’emballage biodégradables par dissolution et pressage à chaud a été examiné. Et puis, des films de cellulose régénérés avec une résistance élevée à la traction et une propriété de barrière à la vapeur d'eau ont été développés. Au chapitre 2, les recherches récentes sur le recyclage des déchets textiles et sur les matériaux fonctionnels dérivés des déchets textiles ont été analysées, qui se sont principalement concentrées sur les trois aspects suivants : (1) gestion des déchets textiles et des matières textiles, (2) les méthodes de recyclage des déchets textiles, et (3) les applications des déchets textiles recyclés dans l’industrie textile, le traitement environnemental, l’électrochimie, les solutions d’ingénierie, les matériaux d’emballage et l’extraction de micro/nano-cellulose. Au chapitre 3, la dissolution et la régénération de déchets de tissus en coton-élastane dans les systèmes de solvants H_2SO_4, NaOH/urée et LiCl/DMAc a été étudié. Tous les trois systèmes de solvants pourraient efficacement dissoudre les fibres de cellulose tout en produisant des formes différentes de composants d'élasthanne. Les fibres d'élastane étaient incapables de se dissoudre dans le solvant NaOH/urée, mais elles ont été partiellement dissoutes dans le solvant H_2SO_4 et complètement dissoutes dans le solvant LiCl/DMAc. Les films produits à partir du système de solvant LiCl/DMAc ont obtenu les meilleures propriétés de transparence, de résistance à la traction et de barrière à la vapeur d'eau, grâce à la dissolution complète des fibres d'élasthanne. Au chapitre 4, le pressage à chaud a été utilisé pour les films composites de cellulose régénéréé, qui ont été préparés avec trois systèmes de solvants à des pressions et températures différentes. Les films composites de cellulose régénérée ont été pressés à chaud à 120 °C/180 °C et 4,45 MPa/44,5 MPa pendant 15 minutes. Les résultats ont révélé que la résistance à la traction et le module de Young augmentaient à une température de pressage à chaud plus élevée, mais n'étaient pas affectés par l'augmentation de la pression de pressage à chaud. La propriété de barrière à la vapeur d'eau des films de cellulose régénérée a également pu être améliorée, mais une amélioration supplémentaire à une température de pressage à chaud élevée n'a été constatée que pour les films préparés par le système NaOH/urée. De plus, les films composites de cellulose régénérée préparés à partir du système LiCl/DMAc pressé à chaud à 180 °C et 4,45 MPa ont présenté la résistance à la traction la plus élevée (202,10 ± 6,82 MPa), le module de Young le plus élevé (12,79 ± 1,11 GPa) et la PVW la plus faible (2,89 ± 0,37 × 10^{-8} g m^{-1} h^{-1} Pa^{-1}). En résumé, cette recherche démontre que les déchets textiles contenant des fibres de coton et d'élasthanne peuvent être recyclés et pressés à chaud en films de cellulose régénérés, qui ont des applications potentielles comme matériaux d'emballage. De plus, cette recherche fournit une stratégie prometteuse pour soulager la pression environnementale causée par les déchets textiles.

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CONTRIBUTION OF AUTHORS

This thesis is edited in a manuscript format and consists of five chapters. Chapter 1 presents a general introduction that includes a brief overview of the recent relevant work in the literature and describes the research objectives presented in the thesis. Chapter 2 reviews the research on the recycling of textile wastes and the applications of the derived functional materials in recent five years. Chapter 3 investigates the dissolution of waste cotton textiles containing elastane fibers in three solvent systems and the properties of regenerated cellulose films and has been published in the journal Membranes. Chapter 4 examines the structure, mechanical properties, water vapor barrier property, and thermal stability of hot-pressed regenerated cellulose films prepared from three solvent systems. Finally, Chapter 5 presents the overall conclusion of the thesis, as well as some suggestions for future research.

The present author, Luxuan Wang, was responsible for the experimental work, data acquisition and analysis, and writing of the thesis. Dr. Yixiang Wang, the thesis supervisor, guided the research and revised the thesis prior to the submission. Shuting Huang was responsible for reviewing and revising Chapter 3.

PUBLICATIONS

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LIST OF ABBREVIATIONS

$(CH_3CO)_2O$:	Acetic anhydride
[Amim]Cl:	1-Allyl-3-methylimidazolium chloride
[BMIM][Ac]:	1-Butyl-3-Methylimidazolium Acetate
[Bmim]OAc:	1-Butyl-3-methylimidazolium acetate proionic
[DBNH]OAc:	1,5-diazabicyclo[4.3.0]non-5-ene acetate
ABC:	Acidochromic regenerated cellulose
AC:	Activated carbon
ACC:	All-cellulose composite
Ag@HPAMAM:	Hyperbranched polyamide-amine silver nanoparticles
ANOVA:	Analysis of variance
BHET:	Bis(2-hydroxyethyl) terephthalate
Bi_2WO_6:	Bismuth tungstate
BTBAC:	Benzyltributylammonium chloride
$BzMe_3NOH$:	Benzyltrimethyl ammonium hydroxide
$CaCl_2$:	Calcium chloride
CD:	Cross direction
CNC:	Cellulose nanocrystal
CNF:	cellulose nanofiber
CNT:	carbon nanotubes
CO_2:	Carbon dioxide
DMAc:	N, N-Dimethylacetamide
DMCHA:	N, N-Dimethylcyclohexylamine

DMF:	N, N-dimethylformamide
DMSO:	Dimethyl sulfoxide
DRC:	Cellulose films prepared from LiCl/DMAc solvent
DTG:	Derivatives of thermograms
EG:	Ethylene glycol
EPI:	Epichlorohydrin
FPU:	Filter paper unit
FT-IR:	Fourier transform infrared spectroscopy
GO-ODA:	Graphene oxide modified by chemically grafting octadecylamine
H_2O:	Water
H_2SO_4:	Sulphuric acid
H_3PO_4:	Phosphoric acid
HCl:	Hydrogen chloride
HNO_3:	Nitric acid
HPW:	Phosphotungstic acid
HRC:	Cellulose films prepared from H_2SO_4 aqueous solvent
ILs:	Ionic liquids
JFRP:	Jute fiber reinforced polymer
$LaFeO_3$:	Lanthanum ferrite
LED:	Light-emitting diode
LiCl:	Lithium chloride
LiOH:	Lithium hydroxide
LMPET:	Low-melting poly(ethyl benzene-1,4-dicarboxylate)
MB:	Methylene blue

MCC:	Microcrystalline cellulose
MD:	Machine direction
N/A:	Not applicable
N_2:	Nitrogen
Na_2CO_3:	Sodium carbonate
NaBr:	Sodium bromide
NaCl:	Sodium chloride
NaClO:	Sodium hypochlorite
$NaClO_2$:	Sodium chlorite
$NaIO_4$:	Sodium periodate
NaOH:	Sodium hydroxide
Ni:	Nickel
NiFe:	Nickel-iron
NIR:	Near-infrared
NMR:	Nuclear magnetic resonance
NPs:	Nanoparticles
NRC:	Cellulose films prepared from NaOH/urea aqueous solvent
NS/PU:	Nylon/Spandex
O_2:	Oxygen
PEDOT:PSS:	Poly(3,4-ethylenedioxythiophene):polyelectrolyte poly(styrenesulfonate)
PET:	Poly(ethylene terephthalate)
PLA:	Poly(lactic acid)
PP:	Polypropylene
PVA:	Polyvinyl alcohol

RC:	Regenerated cellulose
RH:	Relative humidity
RhB:	Rhodamine b
SEM:	Scanning electron microscope
SFRC:	Sisal fiber reinforced concrete
SiO_2:	Silicon dioxide
SPI:	Soybean protein isolate
STPP:	Sodium tripolyphosphate
TEMPO:	2,2,6,6-tetramethylpiperidine 1-oxy
TFA:	Trifluoroacetic acid
TGA:	Thermogravimetric analysis
TiO_2:	Titanium dioxide
TIM:	Thermal interface material
T_{max}:	The maximum decomposition temperature
TOCN:	TEMPO-cellulose nanofibers
TPA:	Terephthalic acid
TPU:	Thermoplastic polyurethane
U:	International unit
UV:	Ultraviolet
VARTM:	Vacuum-assisted resin transfer molding method
VTMS:	Vinyl trimethoxy silane
WVP:	Water vapor permeability
$ZnCl_2$:	Zinc chloride
Zn-CO:	Zinc monocarbonate

CHAPTER 1. INTRODUCTION

The textile industry has become one of the biggest industries in the world and the second-largest contributor to environmental pollution [1]. In the past decades, clothing has been used in fast fashion and styling resulting in a reduced turnover time of textiles, and an increase in clothing expenditure by 40% was reported in Europe [2]. In 2015, the textile industry was responsible for 79 billion cubic meters of water consumption and 1,715 million tons of CO_2 emissions [3]. Textile wastes include production wastes, pre-consumer wastes, and post-consumer wastes [4], and consist of single- or multi-materials such as cotton, wool, viscose, polyester, elastane, aramid, and so on [5]. The complexity of textile components causes difficulties in textile recycling, and the lack of policies and waste management systems together lead to inefficient textile waste treatment methods such as landfilling and incineration [6]. Therefore, various recycling methods (mechanical methods, thermochemical methods, chemical methods, and enzymatic methods) for textile wastes have been adopted in recent years for value-added applications in the textile industry, environmental treatment, electrochemistry, engineering solutions, packaging materials, and micro-/nano-cellulose extraction.

Cotton textile is the most common textile product on the market and the annual cotton fiber consumption is about 25 million tons [7]. Cotton fabrics consist of more than 90% cellulose and have been phrased for their good moisture absorbency and heat isolation [8]. However, the poor wrinkle resistance and elasticity of cotton fabrics make cotton and synthetic fiber blends better options for clothing due to their lower costs and proper garment properties [9]. Among all synthetic fibers, elastane (also known as spandex) is a typical synthetic elastic fiber. Elastane fiber exhibits a highly reversible extension of 400-800% and has become the prerequisite for fashionable or functional apparel such as outer clothing, leisurewear, and sportswear [10]. Statistics have shown that 80% of clothing sold in the United States contained elastane in 2010 [11]. Elastane consists of 85% segmented thermoplastic polyurethane (TPU) that contains alternating hard segments such as diisocyanate and soft segments such as polyether and polyester [12]. Studies have focused on the recycling of multi-material textiles such as cotton-polyester blends [13], viscose-polyester blends [14], wool-polyester blends [15], and nylon-elastane blends [16]. However, the recycling methods for cotton and elastane fibers have not been fully studied.

Cellulose is one of the most common natural biopolymers, and cotton cellulose has been applied in many applications. For instance, dissolution and regeneration of cotton cellulose into regenerated cellulose (RC) films are commonly used. Extensive research have focused on the solvents of waste cotton textiles, such as H_2SO_4/H_2O, trifluoroacetic acid, phosphoric acid/H_2O, LiOH/urea/H_2O, NaOH/urea/H_2O, LiCl/DMAc, and ionic liquids [17-23]. The rapid dissolution of cellulose has been reported by using H_2SO_4/H_2O and NaOH/urea/H_2O solvents at low temperature [17, 18], while LiCl/DMAc solvent system can also dissolve cellulose without any pre-treatment [23]. However, the dissolution of cotton/elastane fabrics in these solvents has been seldom reported.

Apart from dissolution and regeneration, drying is another key step to meet the desired RC film properties for targeted applications. However, this step evolves complex tasks and may result in uncontrollable side effects that can interfere with the final mechanical performance and physical structure of RC films [24, 25]. Therefore, mitigating the drawbacks caused by drying processes needs to be concerned for optimum material performance [26]. Several drying methods for RC films have been described in the literature including air drying [23], oven drying [27], infrared drying [26], hot pressing drying [28], and press-vacuum drying [29]. Among them, air drying is commonly used, but takes a long time and needs additional control to avoid wrinkling of RC films [26]. Hot-pressing, on the other hand, can reduce the drying time significantly [30], avoid the wrinkling of films, and provide the films with a tight and compact structure simultaneously [28].

In general, the purpose of this study is to recycle cotton/elastane textile wastes into packaging materials with high performance. The objectives of the thesis include two aspects: (1) to study the dissolution of cotton and elastane fibers in H_2SO_4 aqueous solution, NaOH/urea aqueous solution, and LiCl/DMAc solvent systems, and to examine the effect of elastane components on the structure and properties of regenerated cellulose films; and (2) to apply hot-press drying on regenerated cellulose films derived from cotton/elastane fabrics to fabricate packaging materials with improved mechanical and water vapor barrier properties.

CHAPTER 2. LITERATURE REVIEW

2.1 Abstract

The increasing textile industry and resultant textile wastes have attracted more and more attention. Therefore, the recycling of textile wastes into functional materials could be considered a route to relieve environmental pressure and promote socio-economic benefits. The recent research on textile wastes recycling and textile wastes-derived functional materials was reviewed, which mainly focused on the following three aspects: (1) materials and textile wastes management, (2) recycling methods for textile wastes, and (3) applications of recycled textile wastes in the textile industry, environmental treatment, electrochemistry, engineering solutions, packaging materials, and microcrystalline cellulose and cellulose nanocrystal extraction. Textile wastes containing various fiber materials have been recycled with mechanical, thermochemical, chemical, and enzymatical methods into functional materials. However, further efforts are required to establish policies and standardized textile wastes management systems, benchmark design to actual products, and analyze economic and sustainability performance for the scale-up of textile recycling. Finally, future opportunities in the applications of textile wastes-derived functional materials are described.

Keywords: textile wastes, recycling, functional materials, value-added applications

2.2 Introduction

Textile products have been applied in every human activity such as clothing to protect and appearance, home decoration, and transportation utilities [1]. The textile industry has become one of the most important and biggest industries in the world, causing increasing concerns about the consequential environmental impacts. Global fiber production has exceeded 105 million metric tons in 2018 [2], and the global textile and apparel market is predicted to continue growing at a compound average growth rate of 3.7% per year [3]. The impact of the textile industry on the environment mainly comes from the manufacturing process, which uses massive amounts of industrial chemicals and causes the unintentional release of pollutants such as textile fibers into the ecosystems [2]. Textile wastes can come from production waste, pre-consumer waste, and post-consumer waste, and the main risk for textile wastes management pertains to postproduction waste due to a lack of policies and standardized waste management systems [4].

Textiles can be single material based or more commonly multi-material based. Different fiber materials can be found in textiles including natural fibers such as cotton and silk, man-made fibers (e.g. polyester and nylon), and blends of fibers (e.g. cotton/polyester blend and acrylic/wool blend) [5]. Traditional treatments of textile wastes are landfill and incineration. By landfill, the organic substances of textile wastes can be decomposed but may take a lot of space and time (up to 20 years) and may generate toxic substances such as leachate and methane [3]. Waste incineration can recover energy such as electricity or heat but can also generate flue gases (CO_2, H_2O, O_2, N_2) and pose a risk to the environment [4]. Therefore, recycling of textile wastes for value-added applications has been investigated. Among all textile wastes, recycling of cotton, silk, and cotton/polyester blends has been extensively studied [6-9]. Therefore, this review aims to systematically summarize the recycling of textile wastes into functional materials with potential applications in various fields published in the last five years.

2.3 Types of Waste Textiles

Although textile waste has caused increasing concerns, policies and regulations for textile wastes are not available. In order to achieve efficient waste valorization, the efficacy of waste handling and the management of recycling programs are essential [3]. Hole et al. reviewed the policies and incentives for different material recycling and reusing, including metals, paper, glass, and plastics [10]. The challenges for textile wastes recycling and the corresponding possible solutions have been pointed out. As shown in Figure 2.1, most legislation and policies applied to metals, paper, glass, and plastics can be directly implemented in textile recycling and reusing. The policies covering increasing population awareness, reward and tax relief, recycling labeling, separating textile wastes collection, and available collection containers and bins were found viable for the textile industry.

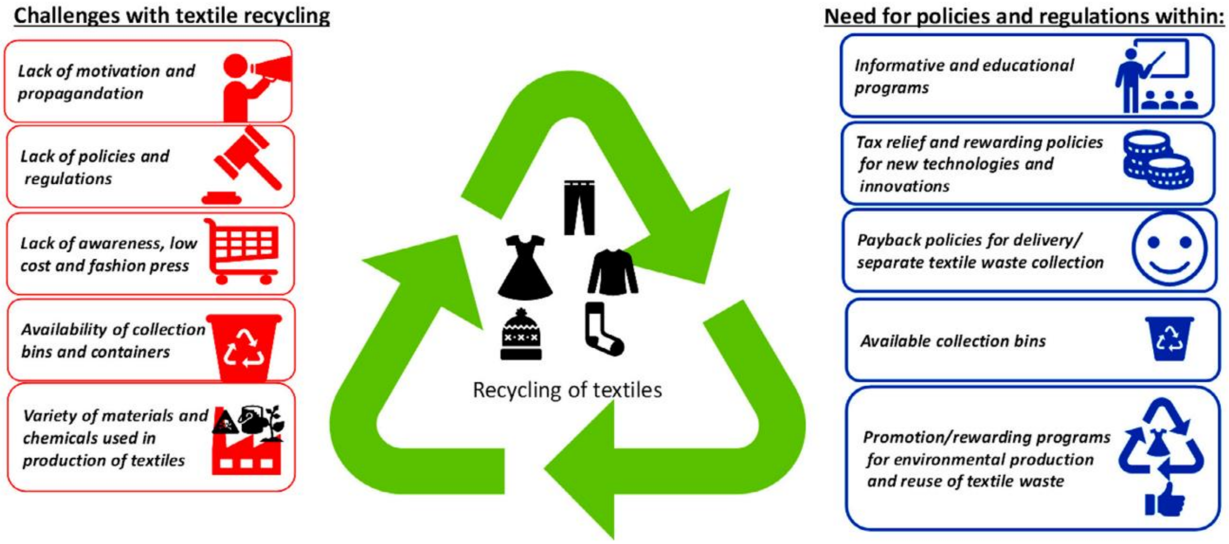

Figure 2.1 Overview over challenges within textile recycling and corresponding possible solutions for introduction of policies [10].

Apart from the policies, a standardized sorting system is essential for defining and assessing the categories and qualities of textile wastes. The study by Nørup et al. established a method for sorting and quality assessment of textiles in household waste [11]. As shown in Figure 2.2, the method consists of sorting with 2 levels followed by 2 levels of quality assessment. At level 1, manually sorting is used to separate textile wastes from other waste. Then, they are separated into clothing (25 types), household textiles (13 types), and several other textiles at level 2. At level 3, 4 steps are required: (1) sorting into products defined for clothing, household textiles, and other textiles and then sorting certain products into further specifications; (2) further sorting by manufacturing method, e.g., knitted fabric, and woven and non-woven textiles; (3) sorting by fabric composition including natural fibers, manmade fibers, and mixed fibers; and (4) assessing the state of the product type for defects, avoidable conditions, and informal use by definition. Step 4 includes a quality assessment of the waste to determine whether it can be reused, recycled, or to be wasted. This method was applied in a case study together with other 5 methods without clear definitions of textile fractions previously established to compare and study its efficiency, and the result demonstrated the importance of a clear definition of the textile fraction.

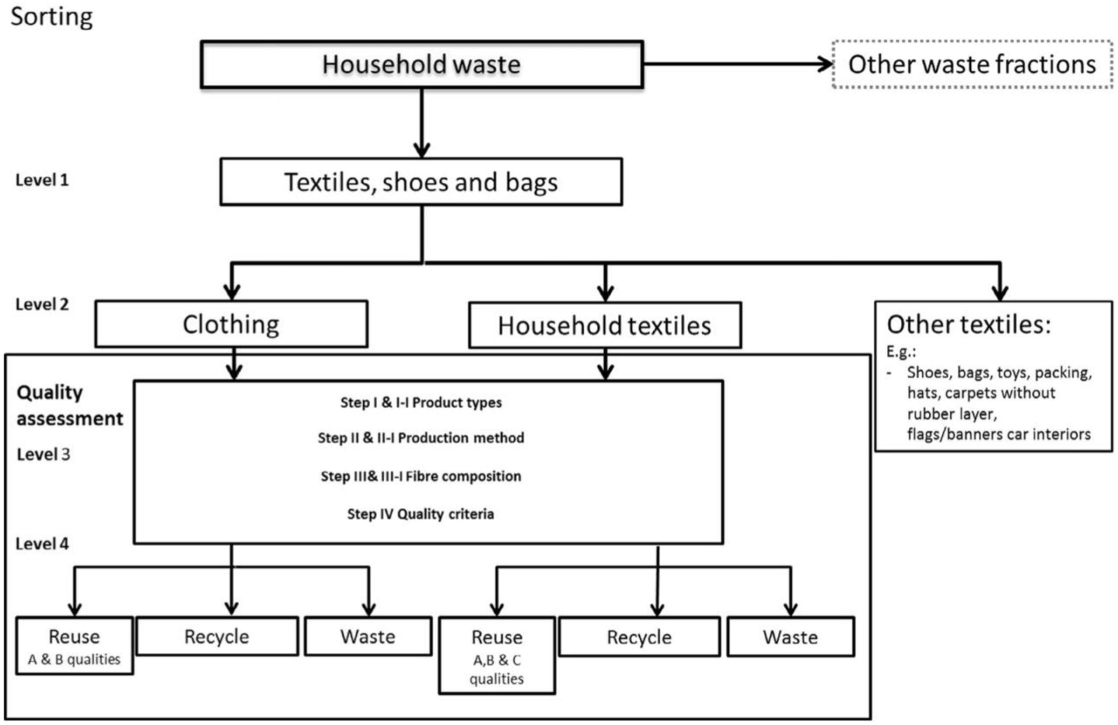

Figure 2.2 Model for sorting and quality assessment of clothing and household textiles [11].

Although the sorting method established by Nørup et al. was a promising management system, the sorting process was done manually, resulting in high cost and low efficiency. Some other sorting methods also have certain limitations. For example, the chemical method can be harmful to the samples, while the currently used physical methods are not sufficient to identify accurately each type of fiber [12]. Therefore, novel technologies are needed to assist in the identification and quantification. Zhou et al. established a fast and accurate classification/identification model using the near-infrared (NIR) spectra modeling technique to study cotton, polyester, polyamide, acrylic, silk, and wool textiles [12]. The results revealed that the recognition rates for cotton and polyester were 93% and 92%, respectively, while the accuracy reached 100% for polyester, polyamide, acrylic, silk, and wool. Liu et al. combined NIR spectroscopy with the convolutional network to automatically classify several common textiles, including pure polyester slash, pure polyester normal, wool, cotton, polyester/nylon, polyester/wool, polyester/cotton slash, polyester/cotton, and nylon [13]. The accuracy rates were all higher than 90%, and the total accuracy rate reached 96%. Both studies showed that NIR technology could be applied to textile wastes recycling with a fast identification speed and a high recognition rate. Apart from NIR, nuclear magnetic resonance (NMR) spectroscopy was also applied in the quantification of cellulose fibers in textile blends. Haslinger et al. used cross-polarization/magic angle spinning NMR to determine the composition of cellulose polyester blends [14]. The calculated concentrations were comparable to the results obtained by acid hydrolysis. In addition, this method was non-destructive and insensitive to different surface structures, colors, and finishing agents applied.

2.3.1 Natural Fibers

Textiles usually consist of different kinds of fibers that can be classified as either man-made fibers or natural fibers [15]. Natural fibers emerge from the textile manufacturing process in a relatively natural state. As shown in Figure 2.3, natural fibers include mineral fibers, animal fibers (e.g., hair and silk), and cellulosic fibers [16]. In 2018, cotton production occupied 80% of natural fiber production by weight. Jute production was about three million tons, and wool production and coir production each accounted for around one million tons [17]. Other specialized natural fibers such as flax, hemp, silk, and sisal fibers added together 1.5 million tons. Natural fibers have been used as raw materials for textile production in prehistoric times, and have been a dominant material in the textile industry for many years until the creation of synthetic fibers in the 1800s [3]. One of the most important properties of woven textiles is comfort. Natural fibers are generally believed to provide better comfort sense than man-made fibers due to their high moisture absorbency, heat isolation, handle, luster, etc [5].

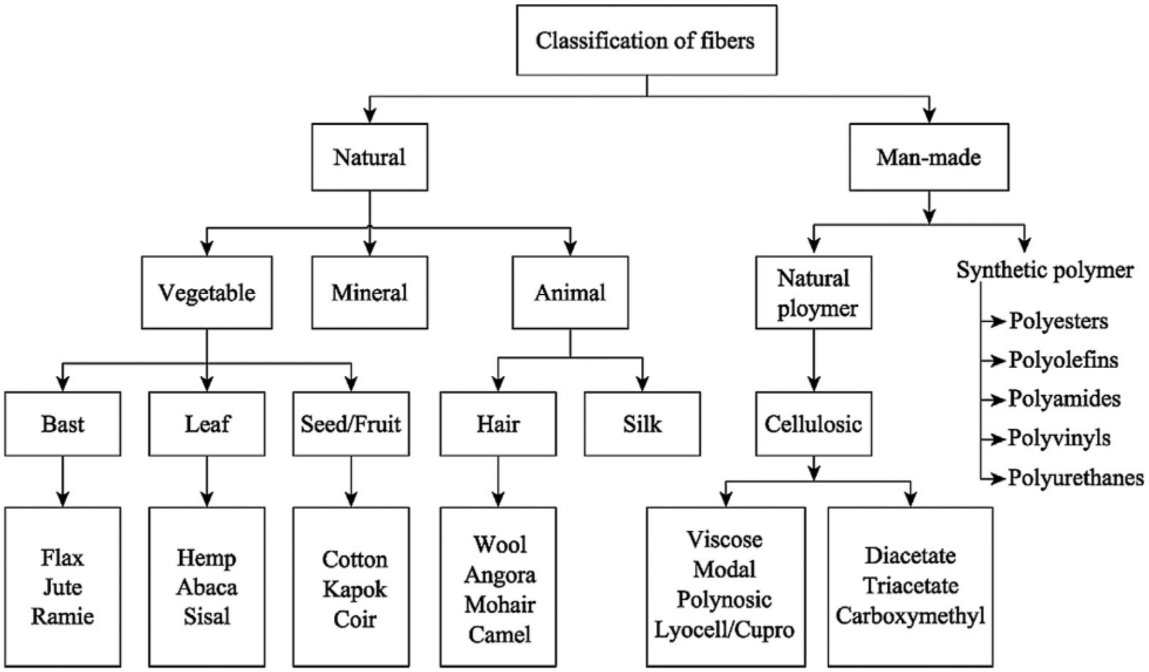

Figure 2.3 Classification of fibers [16].

Cotton is one of the most consumed fibers in the textile industry with about 25 million tons of annual production. The cultivation process of cotton requires a large amount of water, pesticides, insecticides, and fertilizers to obtain high productivity [3]. Cotton contains over 90% of cellulose which makes the cotton fabric strong, soft, durable, comfortable, absorbent, and washable. However, cotton can easily shrink and wrinkle and is expensive compared to man-made fibers. Jute is another important natural cellulosic fiber and is mainly used for sacking and packaging [18]. Jute fibers are stronger and more durable compared with cotton fibers, but they are stiff and less resistant to wrinkle and shred during applications. Wool has a unique thermal comfort property that comes from its high hygroscopicity [5]. It is strong and wrinkle-resistant but is expensive and needs special care (dry wash) during usage. Silk is collected from the cocoon of the silkworm and is known for its luster, strength, lightweight, and elegance.

2.3.2 Man-made Fibers

Unlike natural fibers, the chemical composition, structure, and properties of man-made fibers can be controlled during the manufacturing process. Man-made fibers such as rayon/viscose, lyocell, acrylic, aramid, nylon, polyester, and spandex have been used in garments, home furnishings, and industry products [19]. Man-made fibers can be categorized based on raw materials such as naturally occurring polymers, synthetic organic polymers, and inorganic substances [15]. For example, viscose fibers are made from wood pulp and can provide natural absorbency and softness to nonwoven products [5]. They are commonly used in washing products, medical care, and body protection products. However, the obvious environmental concerns regarding the viscose process limit the production. To address these problems, lyocell was introduced by directly dissolving cellulose in N-methyl-morpholine oxide solvent [15]. Lyocell has been claimed to be “green and eco-friendly” and is widely used in clothes, non-woven, conveyor belts, industrial filter material, and medicine fields [16].

The production of synthetic fibers nowadays is greater than that of natural fibers and obtains increasing concerns with their impact on the environment [3]. Synthetic fibers such as polyester fiber, acrylic fiber, aramid fiber, nylon fiber, and spandex are not praised for their comfort. They cannot provide warmth, adequate bulkiness, softness, thermal isolation, and moisture absorbencies like natural fibers due to their different physical properties and chemical structures. However, synthetic fibers still possess high manufacturing value due to their low cost, high strength, durability, dimension stability, abrasion resistance, thermoplastic properties, and good resistance against heat [5]. Polyester fiber has a leading position among all man-made fibers because it is strong, washable, resistant to wrinkle, fast-drying, cheap, and has good compatibility with other fibers. Poly(ethylene terephthalate) (PET) is the predominant polyester used for fiber production, owing to its good end-use properties, low cost for production, and promising potential for physical and chemical modifications [20]. However, polyester fiber has limitations like poor water absorbability, weak handling, and poor resistance to oily stains [5]. Acrylic fibers are synthetic fibers based on polyacrylonitrile, which are produced by the polymerization of acrylonitrile (vinyl cyanide). Acrylic fibers are soft, light-weighted, warm, non-allergenic, and cheap. Common commercial acrylic fibers are copolymers of acrylonitrile (more than 85%) with other vinyl monomers such as vinyl chloride [15]. Nonetheless, acrylic fibers can be sensitive to heat and may pill with abrasion [5]. Aramids are made of aromatic polyamide fibers that have high strength, inherent flame resistance, and thermal stability [15]. Therefore, they have been widely used in many applications including mountain climbing and mine rescue, fire-resistant clothing, body armor, and spacecraft shielding [21]. Nylon 6 and 66 are the most extensively used nylon materials, which were aliphatic polyamides with high melting points, high strength, and elastic properties

[15]. Spandex/elastane is an elastomeric fiber consisting of at least 85% of segmented polyurethane and has a highly reversible extension (500%) [22].

Table 2.1 summarizes the main properties of most common fibers [5]. Considering their different drawbacks, a mixture of several types of fibers is a suitable solution to modify the properties of garments. A notable example is cotton/polyester blends, where cotton has excellent water absorbency and polyester showed excellent wrinkle resistance. Therefore, the garment made of cotton/polyester blends is water vapor permeable and wrinkle resilient, which requires less ironing and is comfortable and cheaper than pure cotton fabrics. Rayon can also be added to the cotton/polyester blends to improve the shininess. Spandex/elastane fiber, subjected to its stretchability and durability, can be used together with cotton for sports cloth [5]. The wool/polyester blend is also common for winter clothes with a high performance-to-cost ratio and is highly resistant to abrasion and wrinkles. However, a blend of textiles makes them harder to be recycled.

Table 2.1 Major properties of common fibers [5].

Properties	Cotton	Wool	Polyester	Acetate	Rayon	Acrylic	Nylon
Durability	Very good	Moderate	Excellent	Poor	Moderate	Moderate	Excellent
Liquid absorbency	Excellent	Slow/good	Poor	Good	Good	Poor	Poor
Wrinkle resistance	Poor	Excellent	Excellent	Poor	Moderate	Good	Excellent
Care	Machine wash	Dry clean	Machine wash	Dry clean	Machine wash gently	Machine wash	Machine wash

2.4 Recycling Methods

In the past five years, many studies have focused on the recycling of natural fibers, man-made fibers, and fiber blends. Most of them utilized chemical methods to hydrolyze or dissolve textile wastes, especially cellulose-containing materials. Mechanical and thermochemical methods are also very common, while enzymatic recycling is only performed for the recycling of polyester-containing fiber blends.

2.4.1 Recycling of Natural Fibers

2.4.1.1 Recycling of Cotton Fibers

Cotton textile occupies the largest portion of textile products [17], and extensive studies have focused on recycling cotton textiles by using mechanical methods [23], thermochemical methods [24], and chemical methods [25].

For mechanical recycling of cotton textile wastes, Kamble & Behera converted cotton textile wastes into a fibrous form using the rag-tearing technique, followed by transferring it to the fibrous web with a carding machine [26]. The resultant cotton fibrous web was used to develop thermoset composites, which had comparable mechanical properties with that of wood. Baccouch et al. examined the effect of alkaline treatment on the mechanical characteristics of cotton-epoxy composites using carding, needle punching process, and vacuum-assisted resin transfer molding method (VARTM) [27]. The best mechanical properties were obtained for composite panels with cotton mat treated with 1.5M sodium hydroxide (NaOH) for 3 hours. Woven composite fabrics were also used as reinforcing material. For instance, Umar et al. prepared the laminated composites with polyester resin and 8 layers of cotton woven fabrics pretreated with enzymatic desizer using VARTM [23]. The resultant composite material was a substitute for commercial glass fiber composites. Cotton textile wastes were recycled into composite fibers through shredding, mixing with virgin cotton and polyester fibers, and rotor spinning. Ütebay et al. investigated the effect of cotton textile wastes on the quality of recycled fibers by examing the short fiber ratio, recycled fiber length, and spinnability of spinning dope [28]. The results revealed that the properties of yarn were affected by the recycled fiber quality, and the recycled cotton fibers with better quality could be obtained by choosing loosely knitted greige cotton fabrics shredded in 3 passages with large feeding sizes.

Thermochemical recycling methods for cotton textile wastes were investigated to produce activated carbon (AC), biochar, and carbonized cotton fabrics for value-added applications. For instance, Deng et al. decorated cotton fabrics with lanthanum iron oxide ($LaFeO_3$) perovskite followed by calcination at 550 ℃ for 2 hours to acquire the desired fibrous phase of AC [29]. The $LaFeO_3$ perovskite crystals were found growing on the surface of AC and were used for dye removal. Wanassi et al. also produced AC through pyrolysis at 700 ℃ for 1 hour followed by activation with zinc chloride [30]. Biochar was produced by torrefaction at the temperature between 300 and 400 ℃ for 1 hour and was used as fuel [31] and printing material [32]. Carbonized cotton fabrics as a structural material for strain sensors were investigated by Chen et al. through a staged carbonization method, where the temperature was raised to 150 ℃ for 30 min, then increased to 450 ℃ for 30 min, and finally, hold at 750 ℃ for 60 min [33].

Since cotton consists of over 90% of cellulose, various cellulose solvents such as acids [25, 34-40], alkali/urea solutions [25, 41-48], ionic liquids (ILs) [49-51], and lithium chloride (LiCl)/ N,N-Dimethylacetamide (DMAc) solvent [25] were applied to treat cotton waste. Cellulose nanocrystal (CNC) was extracted by using Sulfuric acid (H_2SO_4)/hydrogen chloride (HCl) aqueous solution [38], 60 wt% H_2SO_4 [37], and 2,2,6,6-tetramethylpiperidine 1-oxy (TEMPO) oxidation [40], and microcrystalline cellulose (MCC) was obtained by using phosphotungstic acid (HPW) [36]. For example, Wang et al. utilized mechanical beating and a mixed solution of $H_2SO_4/HCl/H_2O$ with a volume ratio of 3:1:11 to extract CNC from cotton cloth [38]. Zhong et al. extracted CNC from bleached white cotton fabric and indigo-dyed denim fabric using either 60 wt% H_2SO_4 at 45 ℃ for 1hour or TEMPO oxidation at room temperature for 6.5 hours [40]. The yields of CNC extracted from bleached cotton and denim fabrics by acid hydrolysis were 39.6% and 37.8% respectively, while the oxidation led to higher yields of 72.6% and 78.9% respectively. Huang et al. also used acid hydrolysis and oxidation to extract CNC from cotton fabric, and the yields were 90.40% and 60.41%, respectively [37]. Hou et al. extracted MCC with HPW at 140 ℃ for 6 hours and achieved a high yield of 83.4%. Acids were also used to dissolve cotton cellulose to produce regenerated cellulose (RC) materials [36]. Ding et al. dissolved cotton fabrics in pre-cooled 85% phosphoric acid (0.63 w/v) [35], and Zahid et al. used trifluoroacetic acid (TFA) to dissolve cotton fabrics (1 wt%) [39]. A comparison study by Zhou et al. investigated the dissolution and regeneration of different cotton fabrics (t-shirts, bedsheets, and jeans) in pre-cooled H_2SO_4 aqueous solution, pre-cooled NaOH/urea aqueous solution, and LiCl/DMAc solution [25]. It was revealed that three cotton fabrics with appropriate chemical pre-treatments could be rapidly dissolved in H_2SO_4 (2-3 wt%) and NaOH/urea aqueous solution (5 wt%) within 8 minutes, while a longer dissolution time was needed for LiCl/DMAc solution with lower fabric concentration (1 wt%). NaOH/urea and lithium hydroxide (LiOH)/urea solutions were widely utilized for cotton cellulose dissolution [41, 42, 44, 45, 47, 48, 51]. The dissolution of cotton cellulose in benzyltrimethyl ammonium hydroxide ($BzMe_3NOH$) aqueous solution was reported with a relatively high cellulosic solubility of 6 wt% [46]. Cellulose dissolution in ILs has been developed in recent years [50], and pre-treated cotton cellulose was dissolved in 1-Allyl-3-methylimidazolium chloride ([Amim]Cl) [51], 1-Butyl-3-methylimidazolium acetate proionic ([Bmim]OAc): dimethyl sulfoxide (DMSO) [50], and 1,5-diazabicyclo[4.3.0]non-5-ene acetate ([DBNH]OAc) [49] with the solubility of 2.5 w/v, 6 wt%, and 13 wt%, respectively.

Chemical modification on the surface of cotton fibers provides another way to recycle cotton textile wastes. For instance, Araújo et al. modified cotton fibers by acetylation or silanization to improve the interfacial adhesion between the fibers and the matrix [34, 52]. Cotton fabrics were also modified by electrodeposition of metals or metal oxides to make flexible Zinc-Air (Zn-Air) batteries [53]. Table 2 summarizes the common recycling methods for cotton textile wastes.

Table 2.2 Recycling methods for cotton textile wastes.

Matrices / Solvents	Recycling methods	Sample Conc.	Applications	Ref.
Mechanical methods				
Epoxy resin	Compression moulding technique	N/A	Composite panels	[26]
Epoxy resin	Needle punching + VARTM	N/A	Composite panels	[27]
Polyester resin	Weaving + VARTM	N/A	Fiber-reinforced polymer composites	[23]

Virgin cotton 30% + polyester fiber 20%	Shredding + Mixing+ Rotor spinning	50 wt%	Composite fibers	[28]
Thermochemical methods				
N/A	Carbonization	N/A	Flexible strain sensor	[24]
N/A	Torrefaction	N/A	Biochar printed cotton fabric	[32]
$ZnCl_2$ 20 wt%	Pyrolysis	N/A	AC for Alizarin S dye removal	[30]
$LaFeO_3$ sol-gel solution	Calcination	N/A	AC	[29]
Chemical - Acid				
H_2SO_4 + HCl	Hydrolysis	N/A	CNC	[38]
H_2SO_4 + HCl	Hydrolysis + silanization	5 w/v	PLA-cellulose fiber	[34]
H_2SO_4 60 wt%	Hydrolysis	5 wt%	SPI-CNC film	[37]
$NaIO_4$+NaCl --> $NaClO_2$+NaCl+H_2O_2 --> TEMPO+$NaClO_2$+NaClO	Three-step oxidation	N/A		
H_2SO_4 60 wt%	Hydrolysis	5.7 w/v	PVA-CNC film	[40]
TEMPO + NaBr + NaClO	Oxidation	1 w/v	PVA-TOCN film	
H_2SO_4 64 wt%	Hydrolysis	2-3 wt%	RC film	[25]
TFA	Dissolution	1 wt%	RC composite film	[39]
HPW	Hydrolysis	2-5 w/v	MCC	[36]

Phosphoric acid 85 wt%	Hydrolysis	0.63 w/v	PVA/ABC film pH sensors	[35]
Chemical - Base				
NaOH/Urea	Hydrolysis	4 wt%	RC composite film	[44]
NaOH/Urea	Hydrolysis	2.5 wt%	RC composite film	[47]
NaOH/Urea	Hydrolysis	2 wt%	Composite aerogel	[43]
NaOH/Urea	Hydrolysis	5 wt%	RC film	[25]
NaOH/Urea or LiOH/Urea	Hydrolysis	3.25-5 wt%	RC fibers	[42]
NaOH/Urea + $NaIO_4$	Hydrolysis + Oxidization	3.75 w/v	Ag@HPAMAM NPs-embedded cellulose hydrogel	[41]
LiOH/Urea	Hydrolysis	5 wt%	RC composite film	[45]
LiOH/Urea	Hydrolysis	6 wt%	RC composite film & hydrogel	[48]
$BzMe_3NOH$	Hydrolysis	6 wt%	RC composite film	[46]
Chemical - Organic solvent				
LiCl/DMAc	Dissolution	1 wt%	RC film	[25]
Chemical - Ionic liquids				
[DBNH]OAc	Dissolution	13 wt%	Dyed baby jacket	[49]
[DBNH]OAc	Dissolution	2.5 w/v	Composite film for RhB and MB removal	[51]
[Bmim]OAc:DMSO	Dissolution	6 wt%	RC fiber	[50]
Other chemical methods				

$(CH_3CO)_2O/CH_3COOH$	Acetylation	5 w/v	PP-cellulose fiber	[52]
VTMS	Silanization	5-10 w/w		
Ni, Zn, NiFe deposition solutions	Electroless & electro plating/electrochemical deposition	N/A	Zn-Air battery	[53]

Note: $(CH_3CO)_2O$, Acetic anhydride; ABC, Acidochromic regenerated cellulose; Ag@HPAMAM, Hyperbranched polyamide-amine silver nanoparticles; MB, Methylene blue; N/A, Not applicable; NaBr, Sodium bromide; NaCl, Sodium chloride; NaClO, Sodium hypochlorite; $NaClO_2$, Sodium chlorite; $NaIO_4$, Sodium periodate; NPs, Nanoparticles; PLA, Poly(lactic acid); PP, Polypropylene; PVA, Polyvinyl alcohol; RhB, Rhodamine b; SPI, Soybean protein isolate; TOCN, TEMPO-cellulose nanofibers; VTMS, Vinyl-trimethoxysilane; $ZnCl_2$, Zinc chloride; Ni, Nickel; NiFe, Nickel-iron; Zn, Zinc

2.4.1.2 Recycling of Jute Textile Wastes

The use of concrete wrapped with fiber-reinforced polymer has gained attention, and jute is known for its high tensile strength which is comparable to that of glass fiber [54]. Therefore, Tan et al. recycled jute fabrics by mechanical methods to manufacture the sisal fiber reinforced concrete (SFRC) composite column wrapped by jute fiber reinforced polymer (JFRP) [54]. The JFRP was prepared by fixing the unidirectional jute fiber sheets on epoxy-saturated surfaces with paintbrushes or rollers and then wrapped over SFRC. The thermochemical method was also applied to recycle jute, in which the chemical activation by phosphoric acid (H_3PO_4) or $ZnCl_2$ with different concentrations at different temperatures was analyzed [24]. The optimized activation condition by H_3PO_4 was at 700 °C for 90 min with an impregnation ratio of 1.0 while at 500 °C for 60 min by $ZnCl_2$. The resultant AC had a large quantity of randomly distributed pores with varying sizes on the rough surface.

2.4.1.3 Recycling of Protein Fibers

Silk fibers have been recycled by different methods. Liu et al. used silk fabrics as the support body of a graphene-silk pressure sensor through soaking and thermal reduction [55]. Similarly, Ryan et al. dyed silk yarns with conjugated polymer polyelectrolyte complex (PEDOT: PSS) to obtain electrically conductive yarns [56]. Chen et al. degummed silk fibers with sodium carbonate

(Na_2CO_3) and dissolved them in formic acid/calcium chloride ($CaCl_2$) to produce stretchable films [57]. Fibroin precursors were also pyrolyzed to make catalysts [58], and the carbonized silk fabric could be treated with Nitric acid (HNO_3) acid and urea and coated with zinc monocarbonate (Zn-CO) to prepare battery anodes [59]. However, the recycling of wool textiles has been seldom reported in the last five years, where wool fabrics were converted into composite panels by using compression moulding methods together with either a chitosan matrix or a gum Arabic matrix [60].

2.4.2 Recycling of Man-Made Fibers

Viscose and lyocell fibers are produced from cellulose, so similar methods can be utilized to recycle these manufactured fabrics. Nanocellulose (NC) extraction from viscose fibers was reported by hydrolyzing with 64 wt% H_2SO_4 at 40 °C. When the hydrolysis time was longer than 30 min, NC was obtained with an irregular morphology (a weighted average size of 42 nm) and a high crystallinity index of 87% [61]. Viscose fibers were also oxidized by sodium periodate and sodium chlorite and treated by the ball milling technique for dye removal [62], while Lyocell fibers were chemically modified with sodium tripolyphosphate (STPP) for cationic dye adsorption [63]. Synthetic polymer fibers could also be recycled by various methods. For example, polyester textiles were recycled by needle-punching and hot-pressing to make nonwoven hybrid planks with low melting point polyester (LMPET) [64]. Pyrolysis of polyester was carried out between 130 and 900 °C for 0.5 to 1 hour with a catalyst to produce AC [65, 66]. Polyester wastes were also recycled through glycolysis with ethylene glycol into monomer bis(2-hydroxyethyl) terephthalate (BHET) [67, 68] or dissolution with m-cresol [69]. The recycling of aramid fibers was studied by Chuang et al. through needle punching and hot-pressing process to make aramid- LMPET composite boards for protective clothing [70], and acrylic textile wastes were treated by torrefaction to produce cotton fabric ink [32].

2.4.3 Recycling of Fiber Blends

During textile recycling, the major difficulty is the separation of different fiber materials, dyestuffs, and chemicals used in the finishing step. Therefore, apart from commonly used mechanical, thermochemical, and chemical methods, a biological approach with simultaneous recovery of sugars from cotton, keratin from wool, and separation of synthetic fibers like polyester is expected to contribute to the textile waste treatment [71].

2.4.3.1 Recycling of Cotton/polyester Blends

Being the most widely used fiber blend in the textile and apparel industry, cotton/polyester has gained increasing attention in the past five years. Recycling was enabled through the integration of materials by mechanical [72] and thermochemical methods [31] or the separation of cotton/polyester by chemical [73] and enzymatic methods [74].

Post-industrial cotton/polyester (94:6 w/w) waste was recycled by compression moulding technique under heating, and natural rubber was used as the bonding agent to produce sound insulation material [72]. Sharma et al. investigated the fabrication of nonwoven fabrics from cotton/polyester blends with different ratios using needle-punching and calendaring [75]. Torrefaction of cotton/polyester blends was carried out at the temperature of 300-400 ℃ for 1 hour to produce biochar with a high energy yield of 87.01% [31, 32].

Chemical treatments were applied to separate cotton/polyester blends by selective hydrolysis/dissolution of either cotton or polyester content. HPW [73] and H_2SO_4 [76] were reported to hydrolyze cotton fibers while NaOH [77], DMSO [78], and N,N-Dimethylcyclohexylamine (DMCHA) [79] were found to hydrolyze or depolymerize polyester and release cotton fibers. Ling et al. hydrolyzed cotton cellulose into MCC with HPW and the filtrated polyester was mixed with diethyl ether to obtain terephthalic acid (TPA) monomer [73]. Palme et al. utilized benzyltributylammonium chloride (BTBAC) as a catalyst to speed up the hydrolysis of PET and obtain TPA, ethylene glycol (EG), and cotton [77], and Yousef et al. developed a strategy for cotton/polyester fabric recycling at a pilot-scale by dissolving polyester in DMSO [78] or DMCHA [79] with the total recovery rates of about 96% and 93%, respectively. However, the chemical methods reported to separate natural fibers from garments usually used extreme conditions that might affect the mechanical properties [80]. Therefore, enzymatic methods using microbe [74] or commercial cellulase [81, 82] for glucose production and polyester recovery were reported. Hu et al. studied the optimum cellulase production condition by *Aspergillus niger* CKB and the yields of glucose and polyester were 70.2% and 100%, respectively [74]. Li et al. used commercial cellulase (Celluclast) and β-glucosidase (Sunson) to hydrolyze cellulose in blends [81]. The optimum condition was using 20 FPU/g cellulase and 10 U/g β-glucosidase at 50 ℃ and pH 5 with a glucose recovery yield of 98.3% after 96 hours of hydrolysis. A similar condition was studied by Subramanian et al. with commercial cellulase (Novozymes) for a life cycle impact assessment [82]. The recycling methods of cotton/polyester textile wastes are summarized in Table 2.3.

Table 2.3 Recycling methods for cotton/polyester textile wastes.

Matrices / Solvents	**Recycling methods**	**Sample Conc. / Max. Enzyme Activity**	**Applications**	**Ref.**
Mechanical methods				
Cotton-polyester-natural rubber	Compression moulding technique	N/A	Sound insulation material	[72]
Polyester-cellulose	Needle punching + calendaring	70:30, 50:50, 30:70	Cotton/polyester nonwoven fabric	[75]
Thermochemical methods				
N/A	Torrefaction	N/A	Biochar as fuel	[31]
N/A	Torrefaction	N/A	Biochar printed cotton fabric	[32]
Chemical - Acid				
HPW	Cotton hydrolysis	1-2.5 w/v	MCC	[73]
Chemical - Base				
5-15 wt% NaOH + BTBAC catalyst	Polyester hydrolysis	N/A	Cotton fibers and TPA	[77]
Chemical - Organic solvent				
Diethyl ether	Polyester glycolysis	1-2.5 w/v	TPA	[73]
DMSO	Polyester dissolution	N/A	Recovered cotton and polyester	[78]

DMCHA	Polyester dissolution	N/A	Recovered cotton and polyester	[79]
Chemical - Ionic liquids				
[BMIM][Ac]	Cotton dissolution	6 wt%	ACC	[76]
Enzymatic methods				
Aspergillus niger CKB	Cotton enzymatic hydrolysis	1.56 FPU/g	Glucose and polyester	[74]
cellulase + β-glucosidase	Cotton enzymatic hydrolysis	cellulase:10–40 FPU/g β-glucosidase: 0–50 U/g	Glucose and polyester	[81]
Novozymes®	Cotton enzymatic hydrolysis	cellulase: 20 FPU/g; β-glucosidase: 10 U/g	Polyester fibers and glucose syrup	[82]

Note: [BMIM][Ac], 1-butyl-3-methylimidazolium acetate; ACC, All-cellulose composite; FPU, Filter paper unit; U, International unit

2.4.3.2 Recycling of Other Blends

An enzymatic attempt was performed to selectively degrade wool fibers in wool blends. Commercial protease was used and higher weight loss was observed in the presence of sodium thioglycolate as a reducing agent [80]. Cellulase should also be added if wool/cotton/polyester blends were studied [83]. Hanoğlu et al. produced biochar from acrylic blends (acrylic/wool, acrylic/polyester, acrylic/viscose) at the temperature of 300-400℃ [31]. The results showed that the fiber type was responsible for the energy densification ratio and biochar properties. The energy yield decreased with the increase in temperature, and the highest yield for acrylic/wool blend was observed at a torrefaction temperature of 300 °C. Dissanayake et al. recycled nylon/spandex (NS/PU) fabric offcut by compression moulding technique and the best thermal insulation property was achieved when the NS/PU ratio was 60 : 40 [84].

2.5 Applications of Recycled Textile Wastes

The potential applications of recycled textile wastes can be classified into six categories: textile industry [42], environmental treatment [29], electrochemistry [33], engineering solutions [54], packaging materials [25], and MCC and CNC extraction [36], which are shown in Figure 2.4 and summarized in Table 2.4.

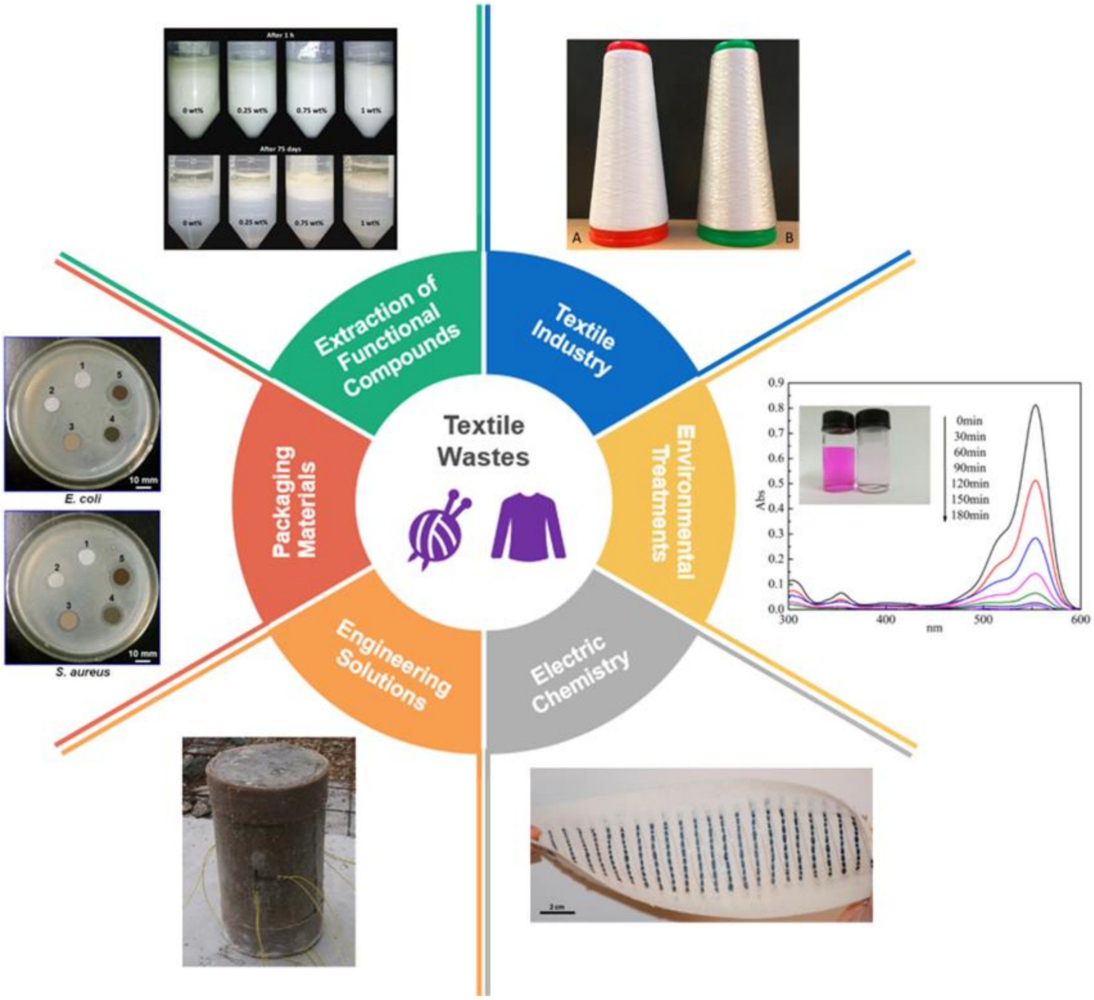

Figure 2.4 Potential applications of recycled textile wastes [41, 51, 54, 56, 61, 67]. © 2020 Elsevier Ltd. All rights reserved; Copyright © 2019, Springer Nature B.V.; Copyright © 2017 American Chemical Society; 2017 Polymer Composites; 2020 American Chemical Society; 2019 Elsevier.

Table 2.4 Potential applications of recycled textile wastes.

Textile wastes	**Recycling methods**	**Applications**	**Ref.**
Textile industry			
RC Fibers	Alkaline hydrolysis - Cellulose	RC fibers	[42]
RC Fibers	Ionic liquid dissolution - Cellulose	RC fibers	[50]
Cotton fibers & polyester	Organic solvent dissolution – polyester	Regenerated cotton fibers and polyester	[78]
Cotton fibers & polyester	Organic solvent dissolution – polyester	Regenerated cotton fibers and polyester	[79]
Cotton fibers	Alkaline hydrolysis – PET, polyester	Cotton fibers and TPA	[77]
PET Fibers	Organic solvent dissolution – PET, polyester	Regenerated PET fibers	[67]
Polyester Fibers	Enzymatic hydrolysis - Cellulose	Regenerated polyester fibers	[80]
Polyester Fibers	Enzymatic hydrolysis - Cellulose	Regenerated polyester fibers	[74]
Polyester Fibers	Enzymatic hydrolysis - Cellulose	Regenerated polyester fibers	[81]
Polyester Fibers	Enzymatic hydrolysis - Cellulose	Regenerated polyester fibers	[82]
Cotton/ polyester composite fibers	Mechanical	Composite fibers	[28]
Textile products (baby jacket & scarf)	Ionic liquid dissolution + dying - Cellulose	Recycled colored new textile products	[49]

Cotton/ polyester composite fabric	Organic solvent dissolution – polyester	Polyester reinforced cotton fabrics	[69]
Cotton/ polyester nonwoven fabric	Mechanical	Ecofriendly fabric in various textiles	[75]
Hybrid fabric composites/boards	Mechanical	Protective clothing	[70]
Hybrid fabric composites	Mechanical	Protective clothing field and geotextiles field	[64]
Fabric additives	Thermochemical	Improve the clothing performance and impart functional properties to textile materials	[32]
Environmental Treatment			
AC	Thermochemical	Adsorption of RhB	[29]
RC Composite film	Ionic liquid dissolution - Cellulose	Composite film for RhB and MB removal	[51]
Adsorbent	Thermochemical	Adsorption for cationic dyes (MB)	[62]
AC	Thermochemical	AC for removal of iodine and MB	[66]
AC	Thermochemical	AC for anionic dye removal such as Alizarin S	[30]
AC	Thermochemical	Highly mesoporous AC	[65]
AC	Thermochemical	Pollutant adsorption	[24]
Adsorbent	Cellulose phosphate modification reaction	Lead adsorption	[63]

Adsorbent	Graft polymerization	Lead adsorption	[85]
Electrochemistry			
Flexible strain sensor	Thermochemical	Flexible strain sensor for monitoring human finger and arm motions	[33]
Pressure sensor	Mechanical	Pressure sensor for high pressure detection (>100 kPa) and weak body signals measurement	[55]
Electrodes	Protein acid plasticization	On-Skin stretchable electrodes	[57]
Electrically conducting yarns	Mechanical	Electrically conducting yarns with potential use for e-textile applications	[56]
Battery anode	Mechanical	Flexible substrates in flexible energy storage devices	[59]
Battery	Electroless & electro plating/electrochemical deposition	Flexible and wearable Zn-Air battery	[53]
Oxygen reaction catalysts	Thermochemical	Highly active and superior stable oxygen reaction catalysts towards next generation energy devices	[58]
Thermal interface materials	Acid hydrolysis - Cellulose	Thermal interface materials in electronic device	[39]
Engineering solutions			

Foamed concrete	Mechanical	Buildings	[86]
Composite concrete column	Mechanical	Buildings	[54]
Composite panels	Mechanical	Construction fields, such as particle boards, plywood and flooring.	[87]
Composite panels	Mechanical	Sound insulation material	[72]
Composite sound absorbing material	Mechanical	Composite sound absorbing materials	[60]
Composite panels	Mechanical	Thermal insulation panel	[84]
Aerogel	Alkaline hydrolysis - Cellulose	Lightweight flame retardant fields	[43]
Composite panels	Mechanical	Automotive and building industries	[27]
Composite fabrics	Mechanical	Structural applications and in the automobile interior	[23]
ACC	Ionic liquid dissolution - Cellulose + mechanical	ACC for automotive interior parts, furniture and indoor construction, sports and leisure equipment	[76]
Composite panels	Mechanical	Automotive components and furniture application	[26]
Packaging materials			
RC film	Acid hydrolysis, alkaline hydrolysis and organic solvent dissolution - Cellulose	Potential applications in food packaging and agriculture	[25]

RC composite film	Alkaline hydrolysis - Cellulose	Membrane technology and packaging	[44]
RC composite film	Alkaline hydrolysis - Cellulose	Potential applications in packaging	[47]
RC composite film	Alkaline hydrolysis - Cellulose	Transparent films with potential application on UV protection	[45]
RC composite film & hydrogel	Alkaline hydrolysis - Cellulose	Next-generation packaging, flexible electronic, and optoelectronic applications	[48]
Antibacterial composite film	Alkaline hydrolysis + Oxidization - Cellulose	Active food packaging	[41]
Mechano-bactericidal ACC film	Hydrolysis - Cellulose	CNC/RC film	[88]
CNC	Acid hydrolysis + Oxidation - Cellulose	CNC/TOCN-reinforced PVA film	[40]
CNC	Acid hydrolysis + Oxidation - Cellulose	CNC-reinforced SPI film	[37]
RC Fibers	Cellulose acetylation/silanization	Reinforcement in polymeric matrices	[52]
RC composite film	Alkaline hydrolysis - Cellulose	Potential in diverse fields such as environmental monitoring and food safety	[46]
pH sensor	Acid hydrolysis - Cellulose	Intelligent food packaging	[35]
Microcrystalline Cellulose and Cellulose Nanocrystal Extraction			
MCC	Acid hydrolysis - Cellulose	MCC	[36]
MCC and TPA	Acid hydrolysis - Cellulose	MCC and TPA	[73]

CNC	Acid hydrolysis - Cellulose	CNC	[38]
CNC	Acid hydrolysis - Cellulose	CNC stabilizer for Pickering emulsions	[61]

Note: UV, ultraviolet

2.5.1 Textile Industry

Ellen MacArthur Foundation proposed four main ambitions for the new textile economy in 2017 [89], which aimed to contribute to a circular textile economy by rethinking the existing factors within the system and capturing opportunities missed by its current linear fate. Customers' awareness of sustainable production has also stimulated the textile industry to accept the circular economy concept, so the textile can re-enter the textile system to maximize the usage of resources [89]. Accordingly, a variety of studies focused on the regeneration of textile fibers or the production of composite fabrics from waste to meet the requirements.

2.5.1.1 Regenerated Fibers

Recently, many studies have focused on the recycling of cotton fibers to save energy and water used during cotton fiber production. For example, Liu et al. dissolved cotton waste in alkali/urea solvent systems and re-spun cellulose fibers [42]. The regenerated fibers had very similar tenacity and competitive elongation compared with commercially available rayon fibers. Similarly, cotton waste was pre-treated by H_2SO_4 and then dissolved in ILs, and the obtained fibers retained 79.5% of the original color and showed similar mechanical strength to commercial viscose fibers [50]. Cotton fibers were also easily separated from cotton/PET fabrics at a pilot-scale by dissolving PET in DMSO or DMCHA solvents [78,79], while Palme et al. hydrolyzed PET with NaOH and BTBAC and achieved up to 97% recovery of cotton cellulose [77].

Synthetic polymer fibers could also be recycled and reused. Guo et al. successfully recycled polyester textile wastes through glycolysis of PET with Mg-Al double oxides pellets into BHET monomer [67]. The generated BHET was then polymerized into polymer melt which showed a very good spinnability and the regenerated PET fibers had comparable quality to virgin fibers. Enzymatic hydrolysis of cotton and wool was also applied to separate polyester fibers from blended fabrics [74, 80-82]. This process was carried out under mild conditions, so it did not affect the shape and structure of polyester.

2.5.1.2 Composite Fabrics

Composite fabrics have been developed from recycled waste for better properties. For example, composite woven fabrics were obtained from padding mangle operation, where dissolved polyester waste was allowed to penetrate cotton fabrics [69]. As a result, doubled tensile strength and enhanced thermal stability of fabrics were achieved with the addition of 9.7% of polyester. Çay et al. employed textile waste-derived biochar as fabric additives, which exhibited improved moisture transfer and accelerated drying process [32]. At the same time, cotton/biochar composite was found to have odor masking properties.

Non-woven textiles prepared from needle-punching and hot-pressing with various components were investigated recently. Sharma et al. studied the properties of fabrics containing different ratios of cotton and polyester fibers [75]. The best combination of 30:70 of cotton and polyester resulted in the maximum tensile strength of 16.84 kg/cm^2 in the machine direction (MD) and 23.60 kg/cm^2 in the cross direction (CD). LMPET-polyester protective nonwoven was developed with 10 wt% LMPET and 90 wt% recycled polyester fibers, which exhibited the highest tensile strength of 38.5 MPa, tearing strength of 1392.8 N/mm, bursting strength of 215.9 kPa, and static stab resistance force of 212.6 N [64]. . Chuang et al. concluded a similar work that 10 wt% LMPET and 90 wt% recycled aramid fibers had the optimal mechanical properties and static puncture resistance [70].

2.5.2 Environmental Treatments

Environmental contaminants such as heavy metals and dyes have gained wide attention [62]. Commercial AC materials have large surface areas and high adsorption capacities and demonstrate strong potential for wastewater treatment, but their applications are limited by the relatively high cost [63]. Therefore, agro-industrial wastes have been employed as low-cost raw materials for the preparation of adsorbents.

2.5.2.1 Dye Removal

Dyes are one of the most significant water pollutants attributed to their variety and massive usage in the textile, leather, paper, plastic, rubber, cosmetic, pharmaceutical, and food industries [62]. Many treatment methods including coagulation, biological degradation, and solvent extraction have been reported to remove dyes from aqueous solutions. Among them, adsorption has become the most practical and economic technique due to its simplicity, flexibility, high efficiency, and cost-effectiveness [62]. AC derived from textile wastes could be applied to remove dyes. Deng et al. decorated AC with $LaFeO_3$ perovskite for adsorption of RhB, and the maximum adsorption capacity reached 182.6 mg/g at 293 K [29]. Yu et al. prepared $ZnCl_2$-activated AC with high adsorption capacities of 1028 and 504 mg/g towards iodine and MB, respectively [66]. Oxidized AC could also adsorb MB with a high percentage removal of 97% at pH 9 [62], while anionic dye Alizarin Red S was removed by $ZnCl_2$-activated AC with a maximum adsorption capacity of 74 mg/g at 25 ℃ and pH 3 [30]. Besides various AC materials, a waste cotton fiber/bismuth tungstate (Bi_2WO_6) composite film was developed to adsorb RhB and MB [51]. The removal efficiencies towards RhB and MB under visible light irradiation achieved 93.73% and 97.04% respectively, and the adsorption capacity was maintained at 89% after four adsorption/desorption cycles.

2.5.2.2 Heavy Metal Adsorption

After chemical modification, cellulosic materials could be used for wastewater lead adsorption. Zhou et al. obtained a cellulose-poly(acrylic acid) composite, which showed 95% lead (II) ion (Pb^{2+}) removal with 10 mg/L initial concentration at pH 6.0-8.0 and a maximum adsorption capacity of 35.7 mg/g [85]. A higher adsorption capacity was reported for STPP modified Lyocell fibers that showed 100% removal efficiency towards Pb^{2+} at initial concentrations up to 300 mg/L [63].

2.5.3 Electrochemistry

Multidisciplinary research interest has been attracted by soft bioelectronics that involves electronic engineering, material science, and biomedical knowledge. Attributed to their applications on the human body, soft bioelectronics have strict requirements for biocompatible components [9]. Therefore, biodegradable and biocompatible cotton and silk textile wastes have gained attention on their potential for wearable electronics or active electronic compounds. For instance, a flexible strain sensor with good conductivity was produced with carbonized cotton and natural rubber latex [33]. The electric resistance of the textile composites changed with the tensile strain and showed a promising capability of monitoring human finger and arm motion as shown in Figure 2.5a&b. Similarly, a highly sensitive pressure sensor was developed by Liu et al. by incorporating graphene into silk fabric [55]. The pressure sensor achieved a sensitivity of 0.4 kPa^{-1} with a high measurement range of 140 kPa and was successfully applied in measuring weak body signals like pulse as shown in Figure 2.5c. Plasticized silk electrodes were also produced by the addition of $CaCl_2$ into silk protein and thin-film metallization [57]. The formation of a wrinkled structure allowed high electrical performance with thin film promised skin conformability as shown in Figure 2.5d. Ryan et al. realized electronically conducting silk yarns dyed with the conjugated polymer: polyelectrolyte complex PEDOT: PSS and showed exceptional wear and wash resistance as shown in Figure 2.5e [56]. Silk-derived biochar was found suitable as a battery anode for lithium-ion batteries with $ZnCo_2O_4$ loaded as shown in Figure 2.5f [59]. Cotton textile wastes were used as structural support for a rechargeable flexible Zn-air battery with a good rate performance and outstanding charge and discharge cycling stability [53] as shown in Figure 2.5g. In addition, an oxygen reaction electrocatalyst was prepared into 2D porous carbon nanosheets based on regenerated silk fibroin with atomically dispersed Fe-N_x-C active sites [58]. The silk-derived carbon nanosheets had demonstrated electrochemical activity toward the oxygen reduction reaction and can be utilized for metal-air batteries as shown in Figure 2.5h. Cellulose-based thermal interface material (TIM) was achieved by dissolving cotton fabrics in TFA and dispersion of graphene nanoplatelets [39]. The TIM pads became electrically conductive with estimated cross-plane thermal conductivity of 5.50 W/mK and an in-plane 2D thermal conductivity was found to be about 800 W/mK.

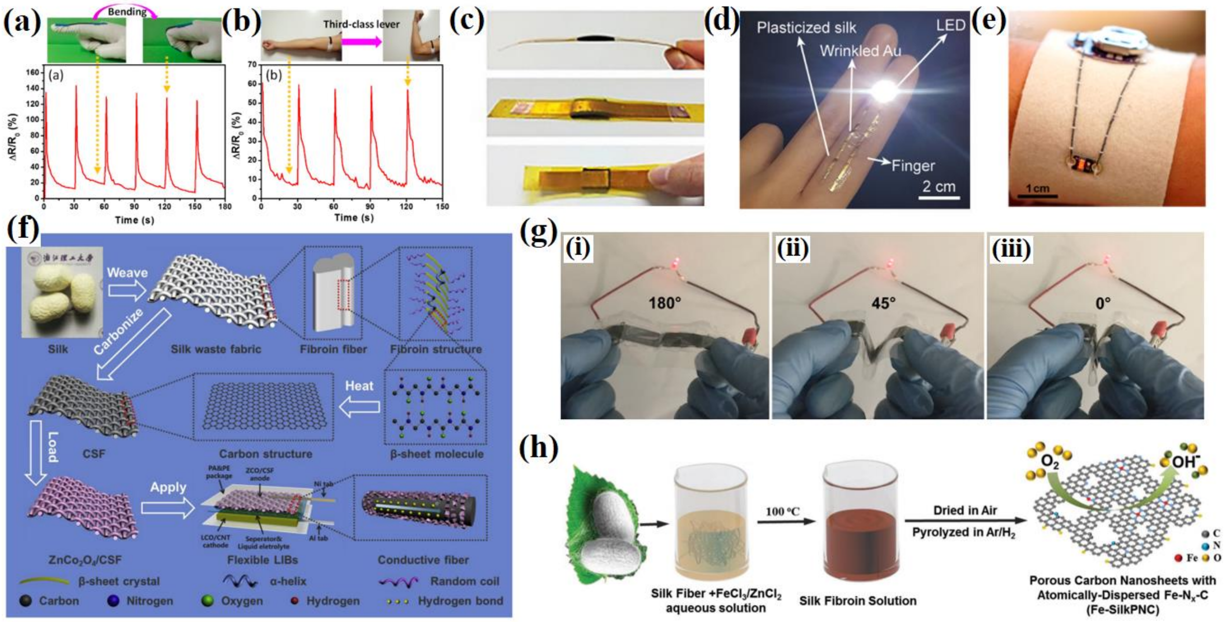

Figure 2.5 Recycled textile wastes in electrochemistry. (a-b) Monitoring pattern of (a) finger bending and (b) contracting of dizzy biceps during third-class lever by using textile composites from the vacuum bagging. Reproduced with permission from ref [33]. Copyright 2019 Polymers. (c) Sample of graphene-silk pressure sensor encapsulated in the Polyimide tape. Reproduced with permission from ref [55]. Copyright 2017 American Institute of Physics. (d) plasticized silk electrodes conformably attached on a finger skin. Reproduced with permission from ref [57]. Copyright 2018 Wiley-VCH. (e) Image of a light-emitting diode (LED) connected with PEDOT: PSS dyed silk yarns to a battery (embroidered on felted wool fabric). Reproduced with permission from ref [56]. Copyright 2017 American Chemical Society. (f) Schematic of CSF preparation and its application to flexible lithium-ion battery. Reproduced with permission from ref [59]. Copyright 2020 Journal of Alloys and Compounds, (g) Photographs of the LED powered by the assembled flexible Zn−air batteries based on cotton textile wastes mechanically bent into different angles of (i) 180°, (ii) 45°, and (iii) 0°. Reproduced with permission from ref [53]. Copyright 2019 American Chemical Society. (h) Preparation process for porous carbon nanosheets with atomically-dispersed Fe–Nx–C oxygen reaction electrocatalyst. Reproduced with permission from ref [58]. Copyright 2019 Wiley-VCH.

2.5.4 Engineering Solutions

Currently, textile wastes have been widely used as reinforcing agents in fiber-polymer composites to replace carbon/glass fibers in engineering applications. In this section, textile wastes were recycled mainly by mechanical methods with low cost, easy process flow, and considerable potential for mass production to manufacture the desired composites [66].

2.5.4.1 Building Materials

In the past five years, textile wastes have gained popularity in building materials such as composite columns [86], composite panels [87], sound insulation materials [60], and thermal insulation materials [84]. Jute fabric wrapped around concrete columns led to a significant increase in compressive strength and ductility [54]. The reinforcing effect increased with the layers of jute wrap and the ultimate increase in compressive strength was 18.4%, 35.7%, and 58.7% for one, three, and five layers of jute fabrics. Textile wastes were also mixed with gypsum in the wet state and the prepared gypsum blocks had a maximum compressive strength of 1.6 MPa with a density of 617 kg/m^3 [86]. Particleboard for flooring was developed from 3D needled textile fiber-epoxy composite with promising peel strength and bearing function [87]. Sound insulation panels comparable to commercial material were produced by Dissanayake et al. from cotton/polyester fabric [72]. Rubino et al. also developed a promising sound-absorbing material from wool fibers [60]. The material showed good sound absorption coefficients that are higher than 0.5 from 500 Hz on and 0.9 from 1kHz on, and a comparable thermal conductivity ranging between 0.049 and 0.060 W m^{-1} K^{-1} to conventional building materials. Thermal insulation material with thermal conductivity of 0.0953 W m^{-1} K^{-1} was obtained by compression moulding nylon/polyurethane fabrics [84]. In addition, a waste cotton fabric/zinc borate composite aerogel was developed by Qin et al. with excellent thermal stability, flame retardancy, and self-extinguishing properties, and might extend the use of cellulose aerogel toward lightweight flame retardant fields [43].

2.5.4.2 Automotive Applications

Recently, the VARTM technique has been widely studied in the production of composite materials based on textile wastes and polymer matrices to substitute inorganic fibers due to their biodegradability, reduced energy consumption, low cost, low density, and comparable mechanical properties [27]. For instance, epoxy-cellulose composite [27], Polyester-cellulose composite [23], and all cellulose composite [76] were found with suitable mechanical properties to be applied to automotive interior parts where lightness and low mechanical stresses were required. In addition, epoxy-cellulose thermoset composite panels prepared with compression moulding technique obtained qualified mechanical properties to replace timber in furniture material and automotive components [26].

2.5.5 Packaging Materials

Various cellulose solvents were developed for the production of RC films and RC composite films. These films showed promising properties for applications in biodegradable packaging, active packaging, and intelligent packaging [90].

Cotton-based RC films were extensively studied and RC composite films with various additives were investigated to examine their mechanical, optical, and barrier properties. Zhou et al. recycled three cotton textiles with H_2SO_4 aqueous solvent, NaOH/urea solvent, and LiCl/DMAc solvent [25]. The types of cotton fabrics did not have a significant impact on the mechanical, thermal, and barrier properties of the recycled RC films, and the RC films prepared from NaOH/urea solution exhibited the highest tensile strength of 76.21 ± 8.26 MPa, the maximum decomposition temperature of 325.66 ℃, and the lowest WVP of $0.81 \pm 0.10 \times 10^{-7}$ g m^{-1} h^{-1} Pa^{-1}. The incorporation of 2 wt% nano-silicon dioxide (SiO_2)was found to increase the tensile strength and modulus of RC films by 26% and 15% and decrease the WVP by 22% [44]. Hydrophobic graphene oxide modified by chemically grafting octadecylamine (GO-ODA) was also applied to enhance the water vapor barrier performance of RC films with more than 20% reduction of WVP achieved by 2 wt% loading of GO-ODA [47]. The UV shielding property of RC films was improved by the incorporation of 2.95 wt% CeO_2 nanoparticles [45], and ultrahigh tough (41.1 MJ m^{-3}) and super clear RC films were fabricated from epichlorohydrin (EPI) crosslinked anisotropic hydrogels with pre-stretching [48]. Ding et al. added the acidochromic dye 1-hydroxy-4-[4-(ethylsulfurate sulfonyl)phenylazo]-naphthalene (HESPN) in RC solution and then mixed it with PVA solution to produce pH sensor [35]. The sensor was able to change color from yellow to purple when pH varied between 5 and 12 with excellent reversibility. In addition, RC composite film exhibited iodide identifying optical sensing property with the addition of Ag nanoparticles [46].

Antimicrobial RC composite films have potential applications in active food packaging to inhibit the growth of food-borne bacteria. Gu et al. incorporated Ag@HPAMAM NPs into RC films, which could inhibit the growth of *Escherichia coli* and *Staphylococcus aureus* and effectively extend the shelf life of cherry tomatoes [41]. It was found that CNC deposited on the surface of RC films could enable the mechano-bactericidal activity towards *Escherichia coli* and *Listeria monocytogenes*, and improve the tensile strength (131.44 MPa) and Young's modulus (5704.33 MPa) of RC films [88]. Waste cotton fibers can also be applied as additives in packaging materials. For instance, Araújo et al. developed a PP-based composite reinforced by cellulose fibers [52].

2.5.6 Microcrystalline Cellulose and Cellulose Nanocrystal Extraction

Cotton textile wastes are promising raw materials for the extraction of MCC [36] and CNC [38]. MCC is partially hydrolyzed and depolymerized cellulose that can be widely used in packaging, agriculture, food, automotive, aerospace, and other industries [73]. MCC was extracted by HPW hydrolysis from pure cotton [36] with a high yield and crystallinity index (CI) of 83.4% and 85.2%, while the yield and CI of MCC obtained from cotton/polyester wastes were 85.1% and 79.6% [73]. Further hydrolysis can result in the production of CNC, which has been applied in the fields of nanocomposites, food packaging, and drug delivery [61]. Prado et al. prepared CNC from viscose yarn waste by using H_2SO_4 hydrolysis, which showed a high CI of 87% and irregular morphology with a weighted average size of 42 nm [61]. A mixed acid solution (H_2SO_4/HCl/H_2O) was also used to extract CNC from cotton cloth, and the CI value of CNC was 55.76% [38]. In addition, Huang et al. and Zhong et al. extracted CNC from waste cotton fibers and used them to improve the mechanical properties of SPI [37] and PVA [40] films.

2.6 Summary and Outlook

In this review, various approaches (mechanical, chemical, thermochemical, and enzymatic methods) to recycling textile wastes have been presented. Instead of conventional treatments such as incineration and landfill, recent research focused on up-recycling of textile wastes into value-added functional materials for potential applications in the textile industry, environmental treatment, electrochemistry, engineering solutions, packaging materials, and extraction of micro-/nano-cellulose. Especially, mechanical treatments such as needle-punching, VARTM, and hot-pressing were applied to make protective clothing, building materials, and automotive devices. Thermochemical treatment and chemical modification of textile wastes allowed the preparation of AC and adsorbents for wastewater treatment, as well as wearable electronics and electronic devices.

It is widely believed that textile recycling is of great importance from socio-economic and environmental aspects. However, despite the recent development of textile wastes recycling, challenges remain in promoting their practical applications:

1. Globally, massive textile wastes are produced yet the reuse and recycling are still poor partly due to the lack of policy, incentives, and textile wastes management system to motivate and navigate end users. Therefore, applicable policies such as reward and tax relief policies, recycling labeling, and separate textile wastes collection can be implemented for large-scale textile recycling. Also, a systematic sorting method for textiles including textile types, textile compositions, and chemicals used during textile production should be taken care of before the recycling process.

2. The development of the functional materials should be associated with specific applications. Most studies only focused on improving the properties of functional materials. However, the desired properties were not linked to any real applications.

3. Economic and sustainable approaches for the recycling of textile wastes are expected in the future, especially for the implementation on an industrial scale. In addition, the economic and sustainability performance of different recycling methods should be analyzed to highlight the estimated economic returns and reduction of carbon footprint.

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CONNECTING STATEMENT I

Chapter 2 reviewed the development of the recycling of textile wastes into functional materials in the last five years. This review covered recent progress in textile waste management, recycling methods (e.g., mechanical methods, thermochemical methods, chemical methods, and enzymatic methods) for different textile materials, and potential applications of functional materials in the textile industry, environmental treatment, electrochemistry, engineering solutions, packaging materials, and extraction of micro-/nano-cellulose. **Chapter 3** investigated the dissolution of cotton textiles containing elastane fibers in three solvent systems, namely H_2SO_4/H_2O, NaOH/urea/H_2O, and LiCl/DMAc solvents. The effect of elastane fibers on the structure and properties (e.g., mechanical properties, thermal stability, and water vapor permeability) of RC films was studied in detail.

CHAPTER 3. RECYCLING OF WASTE COTTON TEXTILE CONTAINING ELASTANE FIBERS THROUGH DISSOLUTION AND REGENERATION

3.1 Abstract

Increasing utilization of textiles has raised concern regarding the environmental impact brought by the textile manufacturing process and disposal of waste textiles. In our previous work, the dissolution of cotton waste through different solvent systems was demonstrated. Herein, this study aimed to further investigate the recycling of waste cotton–elastane fabrics using H_2SO_4, NaOH/urea, and LiCl/DMAc solvent systems. The structure of regenerated films was characterized with Fourier transform infrared spectroscopy and scanning electron microscopy, and the properties of the regenerated films, including transparency, mechanical properties, water vapor permeability, and thermal stability, were investigated. The results revealed that all solvent systems could convert the waste cotton–elastane fabrics into regenerated films with the existence of different forms of elastane components. The elastane fibers were partially hydrolyzed in H_2SO_4 solvent and reduced the transparency of regenerated films, but they were well retained in NaOH/urea solvent and interrupted the structure of regenerated cellulose films. It is worth noting that the elastane fibers were completely dissolved in LiCl/DMAc solvent and formed a composite structure with cellulose, leading to obviously improved tensile strength (from 51.00 to 121.63 MPa) and water barrier property (from 3.50×10^{-7} to 1.03×10^{-7} g m^{-1} h^{-1} Pa^{-1}). Therefore, this work demonstrates the possibility to directly recycle waste cotton–elastane fabrics through dissolution and regeneration, and the resultant films have potential applications as packaging materials.

Keywords: waste cotton textile; elastane fiber; recycling; dissolution; regeneration

3.2 Introduction

Owing to the growing global population alongside the increasing demand for clothing, the textile industry has become one of the most important and biggest industries in the world [1]. In 2018, global fiber production has exceeded 105 million metric tons [1,2]. Conventional treatments of waste textile include municipal landfill and incineration. For landfills, large space is occupied, and the decomposing period can range from 6 months to 20 years depending on the fiber types [1], while incineration may produce harmful substances such as dioxins during a high-temperature process that can accumulate in the environment and food chain [3]. Cotton fiber is one of the most common fibers for textiles [4]. Cotton fabrics have good moisture absorbency and heat isolation but also have poor wrinkle resistance and elasticity [5]. Therefore, synthetic polymeric fibers are usually mixed with cotton fibers to obtain proper garment properties [6]. Among them, elastane (also known as spandex) is a typical synthetic elastic fiber that exhibits a highly reversible extension of 400–800% [7]. Due to its high elasticity, elastane has become the prerequisite for fashionable or functional apparel such as outer clothing, leisurewear, underwear, and sportswear, and it has a 30–40% growth in worldwide consumption per year [8]. In 2010, an estimated 80% of clothing sold in the United States contained elastane [9]. In chemical terms, elastane is a synthetic macromolecule with at least 85% of segmented thermoplastic polyurethane (TPU) [7], in which a hard segment contains diisocyanate and short diol chain extender residues responsible for the stiffness and toughness and a soft segment contains polyols such as polyether and polyester responsible for the resilience, extensibility, and flexibility of polyurethane [10]. Recent studies focused on the recycling of multi-material textiles such as cotton–polyester blends [11], viscose–polyester blends [12], wool–polyester blends [13], nylon–cotton blends [14], and nylon–elastane blends [15]. However, the research on the blend of cotton and elastane fibers has been seldom reported. Moreover, many studies involved at least two steps, separation and reuse; for example, Navone et al. [13] performed enzymatic digestion of wool fibers to recover polyester fibers from wool–polyester blends. It will be more convenient and cost-effective if the blended fibers can be recycled in one treatment.

Cellulose is one of the most important natural biopolymers, which can be used in various fields [16,17]. Dissolution and regeneration of waste cotton fabrics is a convenient way to fabricate cellulose films. Several solvent systems have been reported to dissolve waste cotton fibers, such as LiOH/urea/H_2O, NaOH/urea/H_2O, phosphoric acid/H_2O, H_2SO_4/H_2O, lithium chloride (LiCl)/N, N-dimethylacetamide (DMAc), organic electrolyte solution/ionic liquid system, and ionic liquids [18–24]. Among them, H2SO4 aqueous solution is easy to operate and can rapidly dissolve cellulose at low temperature [25]; NaOH/urea aqueous solvent has been reported as an effective and promising system to dissolve cellulose when precooled to −12.0 °C [26]; LiCl/DMAc is also a well-known cellulose solvent with high stability [27]. Currently, regenerated cellulose (RC) films have been extensively studied for various potential applications in biomedicine [27], packaging [28], thermal management [29], energy storage [30], and optical/electronic devices [31].

In our previous work, three typical waste cotton fabrics (t-shirts, bedsheets, and jeans) were successfully recycled into regenerated cellulose films [24]. Therefore, in this study, we aim to further investigate the dissolution and regeneration of waste cotton– elastane fabrics and study the effect of elastane fibers on the structure and properties of regenerated cellulose films. T-shirts with 95% cotton and 5% elastane were selected to be dissolved in H_2SO_4 aqueous solution, NaOH/urea aqueous solution, or LiCl/DMAc solution. Regenerated cellulose films were obtained from these three solvent systems, and their structures were studied by Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscope (SEM). In addition, the properties of regenerated cellulose films, including transparency, mechanical properties, thermal stability, and water vapor permeability (WVP), were investigated.

3.3 Materials and Methods

3.3.1 Materials

Worn T-shirts (95% cotton/5% elastane) were selected for this research. Sulfuric acid (95.0–98.0%) and sodium hydroxide (≥97.0%) were purchased from Sigma-Aldrich (Oakville, ON, Canada). Acetone (≥99.5%), lithium chloride (≥99.7%), N,N-dimethylacetamide (≥99%), N,N-dimethylformamide (DMF, ≥99.8%), and urea (≥99.6%) were purchased from Fisher Scientific (Ottawa, ON, Canada).

3.3.2 Waste Textile Dissolution and Regeneration

The dissolution and regeneration of waste cotton–elastane fabric were carried out according to our previous work with some modifications [24], and the dissolution conditions in different solvent systems are summarized in Table 3.1. Briefly, the textile was ground (KRUPS, Toronto, ON, Canada) until no fabric pieces could be observed, and the pre-treatment was required for the dissolution in H_2SO_4 and NaOH/urea aqueous solvents. A certain amount of fibers was dissolved with mechanical stirring (IKA Eurostar 60 digital mixer, Wilmington, NC, USA). The obtained solutions were degassed by centrifugation (Eppendorf centrifuge 5430, NRW, Hamburg, Germany) at 3000 rpm for 8 min and then spread on a glass plate and regenerated in coagulation baths. The cellulose films prepared from H_2SO_4 aqueous solvent, NaOH/urea aqueous solvent, and LiCl/DMAc solvent were washed thoroughly with water; dried in air at room temperature; and coded as HRC, NRC, and DRC, respectively.

Table 3.1 Dissolution conditions of waste cotton-elastane fabric in three solvent systems.

Regenerated Films	**Pre-Treatment**	**Solvents**	**Dissolution time**	**Dissolution Temperature (ºC)**	**Fabric Concentration (wt%)**
HRC	48 h in 20% (w/v) H_2SO_4	64% (w/v) H_2SO_4	45 min	0	3
NRC	60 h in 30% (w/v) H_2SO_4	7% NaOH/12% Urea	45 min	0	4
DRC	/	8% LiCl/92% DMAc	3-5 days	80	0.7

3.3.3 Characterization

3.3.3.1 Elastane Fiber Dissolution in Three Solvent Systems

In order to investigate the status of elastane fibers in three solvent systems, the obtained solutions after mechanical stirring were centrifuged at 7830 rpm for 30 min, and the precipitates were separated, washed with water, and freeze-dried (FreeZone Console Freeze dryer 12L, Labconco, Kansas City, MO, USA). They were then characterized by FTIR spectrometer (Cary 630, Agilent Technology, Mississauga, ON, Canada), and the spectra were recorded as the average of 72 scans with 2 cm^{-1} resolution in the 4000–650 cm^{-1} region. The precipitates were also observed by an optical microscope (LMC-1000 Series, Laxco, Mill Creek, WA, USA) equipped with a SeBaCam digital camera (Laxco, Mill Creek, WA, USA).

3.3.3.2 Regenerated Cellulose Film Structure

The structure of regenerated cellulose films was investigated using an FT-IR spectrometer following the same procedure. The morphology of the films with and without DMF treatment was observed by using a Hitachi TM1000 SEM (Schaumburg, IL, USA) at an acceleration voltage of 4 kV. The film samples were sputtered with 4 nm gold–platinum by a Leica EM ACE200 low vacuum coater (Vaughan, ON, Canada) prior to observation and photographing. The films were either directly observed or immersed in DMF for 12 h at room temperature to remove any remaining elastane component and then washed and dried for the observation.

3.3.3.3 Regenerated Cellulose Film Properties

The mechanical properties of regenerated cellulose films (50 mm × 10 mm) were tested on an eXpert 7601 single-column testing machine (ADMET, Norwood, MA, USA) at 25 °C according to standard ASTM D882. The initial grip separation distance was set as 20 mm with a separation speed of 5 mm/min. Three strips with the dimensions of 5 cm × 1 cm (length × width) were cut from each film, and the thickness was determined from SEM cross-section images. All the films were stored and tested at 25 °C and 50% RH. A modified cup method was used to evaluate the WVP of regenerated cellulose films according to ASTM E96-92 standard [32]. The films were sealed in glass jars containing anhydrous calcium chloride. Then, the jars were placed in a desiccator containing distilled water at 25 °C. The weights of the jars were measured periodically, and the WVP of films was calculated using the following equation [32]:

$$WVP = \frac{\Delta m \times k}{A \times \Delta T \times \Delta P} \tag{1}$$

where Δm is the weight change of the jar (g), k is the film thickness (m), A is the exposed area of the film, ΔT represents the time, and ΔP is the partial pressure difference that existed between the two sides of the film (Pa).

Thermogravimetric analysis (TGA) of the regenerated cellulose films was performed using a thermogravimetric analyzer Q500 (TA instruments, New Castle, DE, USA) with a heating rate of 10 °C/min in nitrogen (40 mL/min) from 50 to 600 °C [33]. Thermograms of samples were collected, and the OriginPro software was used for calculating the first derivatives of thermograms (DTG) and the percentage weight loss.

3.3.4 Statistical Analysis

The experiments were carried out in triplicate, and the results were represented as the mean ± standard deviation. Statistical evaluation was carried out by analysis of variance (ANOVA) followed by multiple comparison tests using Duncan's multiple range test. All of the analyses were carried out through SPSS statistical software (IBM, Armonk, NY, USA) with significant differences within samples at $p < 0.05$.

3.4 Results and Discussion

3.4.1 Dissolution of Cotton-Elastane Fabric in Three Solvent Systems

The waste cotton textile containing elastane fibers was dissolved in three solvent systems. Since the capacity of these solvent systems varies, different pre-treatment conditions (sulfuric acid hydrolysis) were introduced to facilitate the dissolution process. The existence of elastane fibers did not show any significant effect on the dissolution of waste cotton fabrics. Similar to our previous work [24], both H_2SO_4 and NaOH/urea aqueous solvent systems required the pre-treatment of acid hydrolysis, while LiCl/DMAc solvent system could directly dissolve the sample after multiple activation steps (e.g., swelled in water and washed with acetone and DMAc). No obvious elastane fibers or aggregates could be distinguished in all three cellulose solutions, and the fabric concentrations in H_2SO_4 and NaOH/urea systems were higher than those in LiCl/DMAc solvent. To better understand the effect of solvent systems on the elastane fibers, the undissolved components were centrifuged out from three cellulose solutions and observed with an optical microscope. As shown in Figure 3.1, some plastic flakes were obtained from H_2SO_4 solution, which might be the partially hydrolyzed elastane under strong acidic condition [34]. It is worth noting that the elastane fibers were well retained in NaOH/urea solvent system but completely dissolved in LiCl/DMAc solution [35].

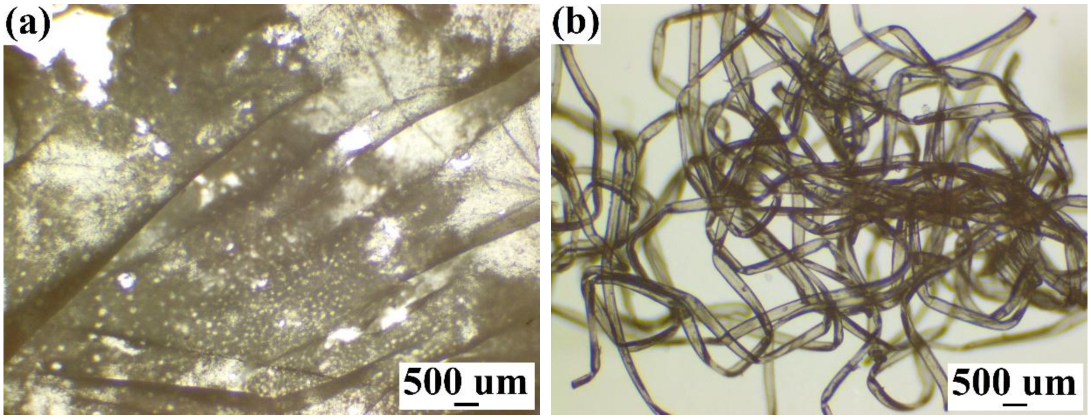

Figure 3.1 Optical microscopic images of undissolved components separated from (a) H_2SO_4 aqueous solvent system and (b) NaOH/urea aqueous solvent system.

3.4.2 Structure of Regenerated Cellulose Films

In order to examine the morphology of regenerated cellulose films prepared from three solvent systems, the SEM images were collected to observe the surfaces and cross-sections of regenerated cellulose films. As shown in Figure 3.2, partial fibers appeared on the surface of HRC film and intact fibers existed on NRC film. Since these components were successfully removed using DMF solvent (highlighted in Figure 3.2c, f), it was confirmed that they were undissolved elastane fibers and were in accordance with Figure 1. In addition, no fibers were found on the surface of the DRC film, and the DMF treatment did not cause any obvious change, which indicated the dissolution of both cotton and elastane fibers by LiCl/DMAc solvent system. Among three regenerated cellulose films, DRC film possessed a relatively smooth and uniform structure with few ripple-like grains that might be contributed by the rapid shrinkage of film during the coagulation process. To be noticed, the surface and inner structure of NRC film were disturbed by the well-retained elastane fibers, which might affect the properties of regenerated cellulose films.

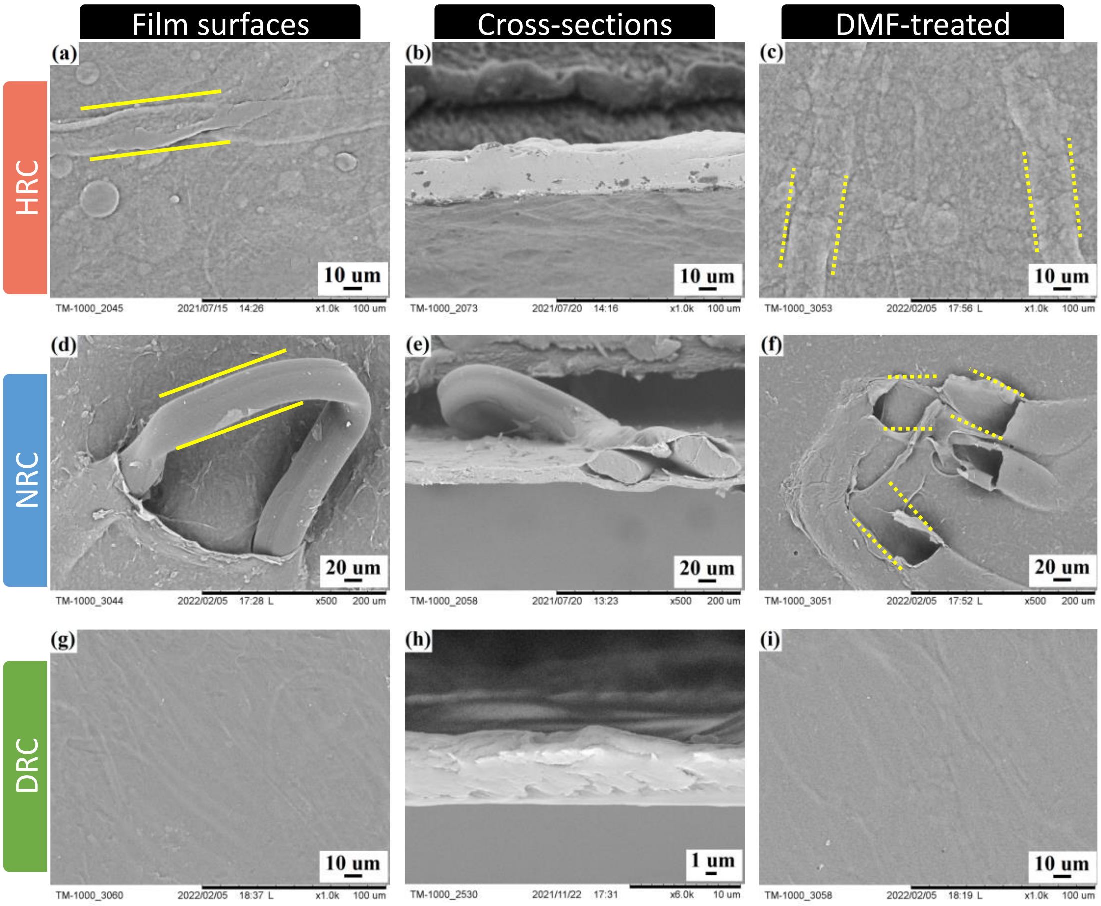

Figure 3.2 SEM images of regenerated cellulose film surfaces (left), cross-sections (middle), and DMF-treated film surfaces (right) prepared from three solvent systems: (a–c) HRC, (d–f) NRC, and (g–i) DRC.

To further investigate the effect of dissolution and the structure of regenerated cellulose films, FT-IR spectra of waste textile, regenerated cellulose films, and undissolved components were collected. As shown in Figure 3.3a, two peaks of waste textile were observed at 3275 cm^{-1} and 3340 cm^{-1} representing the intramolecular hydrogen bonds in cellulose I structure [24]. The peaks at 1431, 1364, 1333, and 1314 cm^{-1} were attributed to CH_2 bending, CH bending, OH bending, and CH_2 rocking vibration, respectively [36]. However, no characteristic peaks of elastane could be found on the spectrum of waste textile, which might be due to the low amount of elastane fibers in the fabric. The change in cellulose crystalline structures after dissolution and regeneration was noticed from the reduction or even disappearance of the characteristic band at 1431 cm^{-1} (Figure

3.3b–d) [36]. In addition, the band at 895 cm^{-1}, representing the amorphous cellulose [37], showed an increase in its intensity. Thus, the band intensity ratio I_{1430}/I_{900} decreased, suggesting that the crystalline structure of cellulose changed from cellulose I to cellulose II [37]. Only NCR film showed a characteristic peak of TPU at 1534 cm^{-1} representing the C-N stretching of amide II [38]. This was because the elastane fibers were retained and exposed on the surface of the NCR film. The undissolved components were also analyzed and are shown in Figure 3.3e, f. In both spectra, a weak peak at 3328 cm^{-1} was attributed to the hydrogen bonds between N-H groups and ester groups (C=O) [39]. Two bands at 1731 cm^{-1} and 1707 cm^{-1} were related to the stretching of free and bonded C=O groups [40]. A characteristic peak of amide II of TPU was found at 1534 cm^{-1}, and a strong band of C-O-C stretching occurred at 1101 cm^{-1}. Therefore, it was confirmed that the undissolved components were mainly elastane components [38].

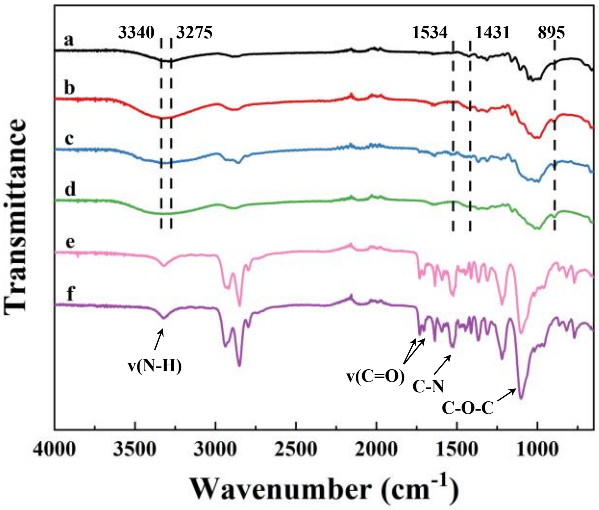

Figure 3.3 FT-IR spectra of (a) cotton-elastane fabrics, (b) HRC, (c) NRC, (d) DRC, and undissolved components separated from (e) H_2SO_4 solvent system and (f) NaOH/urea solvent system.

3.4.3 Properties of Regenerated Cellulose Films

It is evident in Figure 3.4 that all regenerated cellulose films were translucent under room light and natural light. In general, the transparency of regenerated cellulose films is affected by the content of cellulose and the presence of undissolved particles [24]. It has been reported that higher cellulose content could lead to a more compact structure [41]. In addition, undissolved particles can cause optical scattering and internal reflection of light resulting in a decrease in transparency. The DRC film showed better transparency because the content of cellulose in the LiCl/DMAc solvent system was low and the elastane fibers were completely dissolved. However, undissolved elastane components were present in HRC and NRC films and increased the optical scattering.

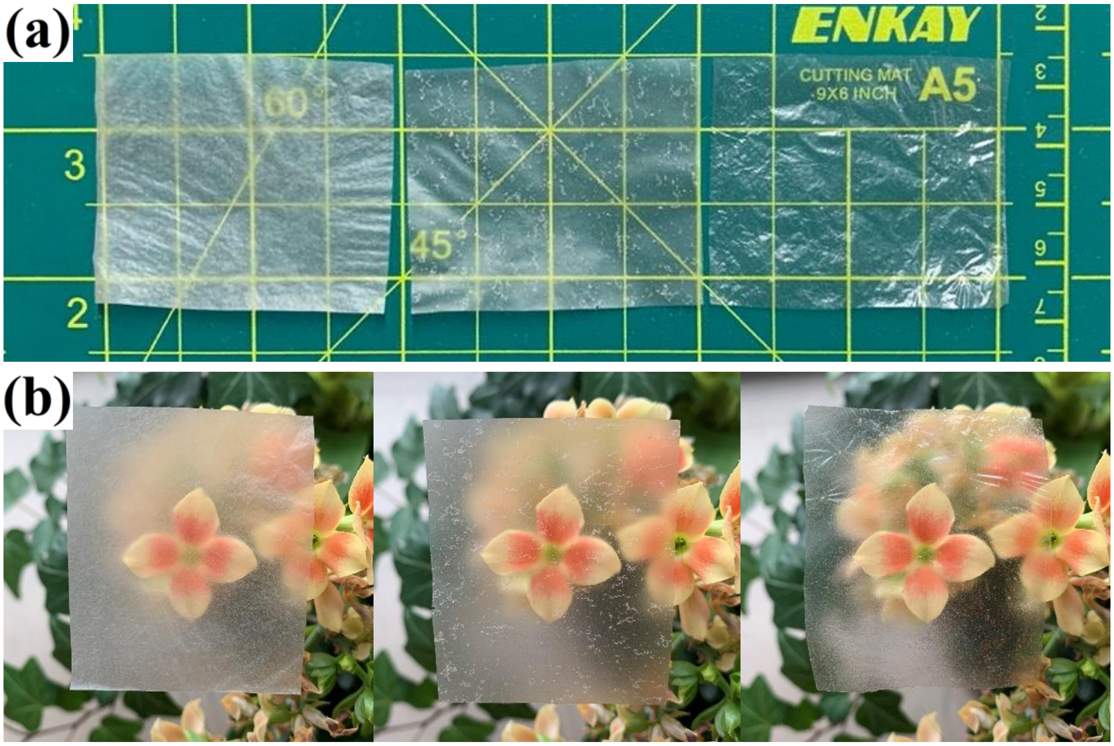

Figure 3.4 Digital pictures of regenerated cellulose films (HRC, NRC, and DRC from left to right) under (a) room light and (b) natural light.

Mechanical properties of regenerated cellulose films are summarized in Table 3.2, and the typical stress–strain curves are shown in Figure 3.5. NRC films exhibited the lowest tensile strength, Young's modulus, and elongation at break among three samples. This might be due to the existence of large undissolved elastane fibers that interrupted the continuity of cellulose film. However, the tensile strengths of HRC and NRC were slightly higher than those of our former regenerated cellulose films from pure cotton textile, while the DRC film was three times stronger than the sample without elastane fibers [24]. This indicated that the elastane component did not have any negative effect on the mechanical properties of regenerated cellulose films, and the dissolved elastane fibers could even reinforce the film by forming a composite structure [42]. WVP values of regenerated cellulose films are also listed in Table 3.2. The DRC film exhibited the best water vapor barrier property ($1.03 \pm 0.53 \times 10^{-7}$ g m^{-1} h^{-1} Pa^{-1}), which was significantly lower than those of HRC and NRC films ($p < 0.05$). This could be due to the dissolved elastane component in DRC film. As shown in Table 3.2, the tensile strength and WVP values of the obtained films were comparable with those of RC films prepared from corncob residue [43], pure cotton textile [24], bamboo [44], and cotton linter [45,46], suggesting that waste cotton–elastane fabric is also a promising source for the preparation of RC films.

Table 3.2 Mechanical properties and water vapor permeability of regenerated cellulose films from various raw materials. Different letters in the same columns indicate the significant difference within this work ($p < 0.05$).

Sample	**Raw Material**	**Solvent Used**	**Tensile Strength (MPa)**	**Elongation at Break (%)**	**Young's Modulus (MPa)**	**WVP (g m^{-1} h^{-1} Pa^{-1})**	**Ref.**
HRC	Cotton-elastane textile	64% H2SO4	67.30 ± 2.82 ^{b}	3.70 ± 0.72 ^{a}	3415.56 ± 89.35 ^{b}	3.50 ± 0.57 × 10-7 ^{a}	This work
NRC	Cotton-elastane textile	NaOH/urea	51.00 ± 1.92 ^{c}	1.49 ± 0.15 ^{b}	3223.08 ± 314.45 ^{b}	2.66 ± 0.32 × 10-7 ^{b}	This work
DRC	Cotton-elastane textile	LiCl/DMAc	121.63 ± 6.16 ^{a}	2.97 ± 0.14 ^{a}	5746.35 ± 343.84 ^{a}	1.03 ± 0.53 × 10-7 ^{c}	This work
RC	Corncob residue	Ionic liquid	70.63	~9.00	-	9.07×10^{-8}	[43]
RC	Bamboo	LiCl/DMAc	81.09	10.98	360	-	[44]
RC	Cotton textile	NaOH/urea	76.21	~3.50	~3250	8.10×10^{-8}	[24]

RC	Cotton linter	NaOH/urea	73.40	5.10	5500	8.21×10^{-6}	[45]
RC	Cotton linter	NaOH/urea	48.34	~2.00	38600	6.16×10^{-7}	[46]

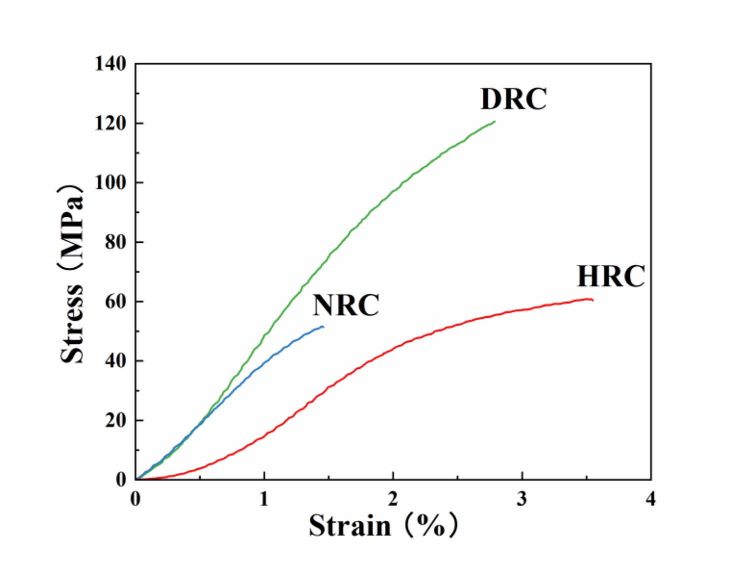

Figure 3.5 Stress-strain curves of regenerated cellulose films from three solvent systems.

TGA and DTG curves are depicted in Figure 3.6. The initial weight loss at about 100 °Cwas due to the dehydration of regenerated films [47]. The main weight loss occurred in the range of 300–390 °C, corresponding to cellulose thermal decomposition and carbonization [33] and urethane hard segment degradation [48]. The maximum decomposition temperatures (T_{max}) of HRC, NRC, and DRC films were 332.68, 360.26, and 359.97 °C, respectively. Among them, the NRC and DRC films exhibited relatively higher T_{max} values, which might be attributed to the higher cellulose concentration in NaOH/urea solution [40] and the dissolution of elastane fibers in LiCl/DMAc solvent [49].

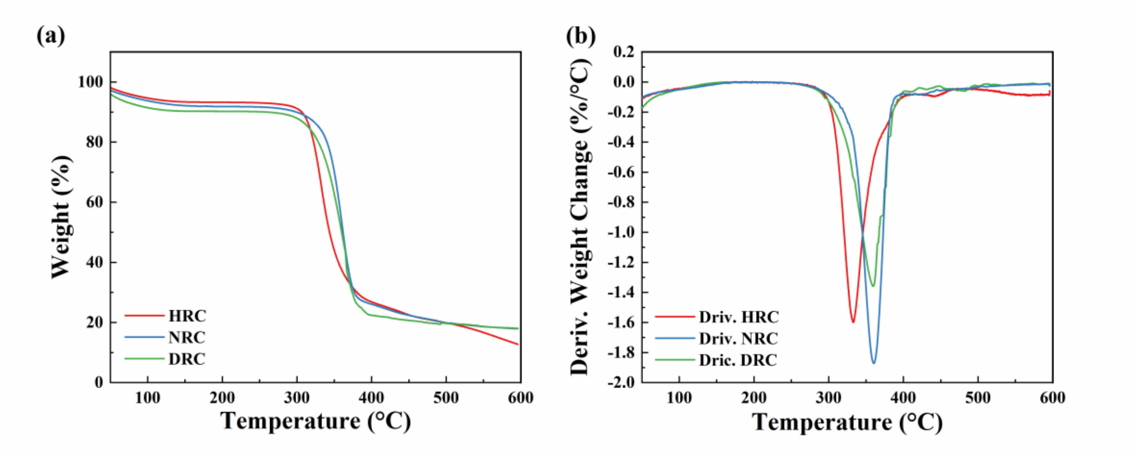

Figure 3.6 (a) Thermogravimetric analysis and (b) derivatives of thermogram curves of regenerated cellulose films prepared from three solvent systems.

3.5 Conclusion

In this work, waste textile containing elastane fibers was successfully converted into regenerated films using H_2SO_4 aqueous solvent, NaOH/urea aqueous solvent, and LiCl/DMAc solvent. All three solvent systems could effectively dissolve the cellulose fibers, while resulting in different forms of elastane components. The NRC film contained large undissolved elastane fibers, and its mechanical properties were weaker than the other two samples. The elastane fibers were partially hydrolyzed in H_2SO_4 solvent but were completely dissolved in LiCl/DMAc solvent, so the DRC film had the uniform structure, high transparency, improved tensile strength of 121.63 ± 6.16 MPa, lowest WVP of $1.03 \pm 0.53 \times 10^{-7}$ g m^{-1} h^{-1} Pa^{-1}, and a maximum decomposition temperature of 359.97 °C. Therefore, it is demonstrated that the waste cotton–elastane fabrics can be recycled by the three solvent systems investigated in this work, which provides a promising strategy to relieve the environmental pressure caused by waste textiles.

3.6 References

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CONNECTING STATEMENT II

In **Chapter 3**, cotton/elastane textile waste was successfully dissolved/dispersed in H_2SO_4 aqueous solvent, NaOH/urea aqueous solvent, and LiCl/DMAc solvent. RC films were regenerated and air-dried, in which different forms of elastane components resulted from three solvent systems that affected the properties of RC films. In **Chapter 4**, the regenerated cotton/elastane films were dried by hot-pressing to trigger a dense film structure. The effects of hot-pressing temperature and pressure on the mechanical properties, thermal stability, and water vapor permeability of RC films were investigated.

CHAPTER 4. IMPROVEMENT OF MECHANICAL AND WATER VAPOR BARRIER PROPERTIES OF REGENERATED CELLULOSE/ELASTANE FILMS BY HOT-PRESSING

4.1 Abstract

The increasing environmental pollution caused by the production and disposal of textiles has raised concerns in recent years. Attention has been attracted to alternative recycling methods for textile wastes instead of landfilling and incineration. In our previous study, cotton textiles containing elastane fibers have been successfully recycled into regenerated cellulose (RC) films using H_2SO_4, NaOH/urea, and LiCl/DMAc solvent systems. In order to rapidly prepare RC films with better performance, in this study, the effect of hot-pressing on the mechanical and water barrier properties of RC films was investigated. The regenerated wet films were compressed at 120 °C/180 °C and 4.45 MPa/44.5 MPa for 15 min. The results revealed that compared to the air-dried samples, the hot-pressing treatment largely improved the mechanical and water vapor barrier properties of regenerated cellulose films. It was worth noting that the tensile strength and Young's modulus increased at the relatively higher hot-pressing temperature, while the different compressive pressures didn't have any significant effect. The RC films prepared from LiCl/DMAc system and hot-pressed at 180 °C and 4.45 MPa showed the highest tensile strength (202.10 ± 6.82 MPa) and Young's modulus (12.79 ± 1.11 GPa), and the lowest water vapor permeability ($2.89 \pm 0.37 \times 10^{-8}$ g m^{-1} h^{-1} Pa^{-1}). Hence, the hot-pressing treatment has promising potential to be applied in the production of regenerated cellulose films with good performance.

Keywords: waste cotton textile, elastane fiber, recycling, hot-pressing, mechanical properties, water vapor barrier

4.2 Introduction

In recent years, clothing has been subjected to fashion and style resulting in rapid growth in the textile industry and reduced turnover time of textiles. For example, in the past few decades, statistics have shown an increase in clothing expenditure by 40% due to fashion changes in Europe [1]. However, the textile industry is ranked as the second-largest contributor to environmental pollution [2]. The contamination can occur during textile manufacturing, usage, and disposal and affect all aspects of the environment encompassing air, land, and water [3]. It was revealed that the textile industry was responsible for 79 billion cubic meters of water consumption and 1715 million tons of CO_2 emissions in 2015 [4]. Textile products penetrated human lives in all aspects such as clothing, furniture, accessories, and home design products [3], which are made from single- or multi-types of materials such as cotton, wool, polyester, nylon, and elastane. During textile production, fabrics with mixed fibers such as cotton/polyester blends, cotton/elastane blends, and silk/linen blends are preferred due to their relatively lower cost and better garment properties compared with single-material based fabrics [5]. However, the recycling of multi-component wastes is much harder than single-material-based textiles, which is due to the different material properties and the difficulties in separation. Although several recent studies have investigated the recycling of multi-material textiles such as cotton-polyester blends [6], wool-polyester blends [7], nylon-elastane blends [8], and acrylic/viscose blends [9], more efforts are needed to better recycle the useful components and reduce the wastes.

The cellulose component in textile wastes is usually recycled by dissolution and regeneration, where various solvent systems are used to form cellulose solutions and then a non-solvent (e.g. water) is employed to regenerate cellulose into a hydrogel film. Therefore, in order to prepare a cellulose packaging film, drying is an essential procedure and can affect the final properties of cellulose films [10]. Several drying methods have been applied to prepare cellulose films including air-drying [11], oven drying [10], hot-pressing [12], and press-vacuum drying [13]. Among them, air-drying is the most used method, which is convenient and does not need any energy input, but it is quite time consuming, and the films may shrink irregularly and result in an uneven surface. Compared to air-drying, the hot-pressing treatment involves high pressure and high temperature, so it can reduce the drying time considerably [14], avoid wrinkling of films, and achieve tight and compact film structure simultaneously [12]. Recently, hot-pressing has been utilized to fabricate various cellulose-based materials such as carbon nanotubes (CNT)/cellulose composites [12], cellulose nanofiber (CNF)/graphite nanoplatelet composites [15], and CNF/TiO_2 composites [16]. Nevertheless, the effect of hot-pressing on regenerated cotton/elastane composites has been seldom reported.

Our previous study has demonstrated the effectiveness of using H_2SO_4, NaOH/urea, and lithium chloride (LiCl)/N,N-dimethylacetamide (DMAc) solvent systems to dissolve cellulose-elastane blends and fabricate RC films. Therefore, in this study, we aimed to investigate the effects of hot-pressing conditions, including hot-pressing temperature and pressure, on the structure and properties of RC films. The structures of hot-pressed RC films were studied by Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscope (SEM), and the mechanical properties, water vapor permeability (WVP), and thermal stability of the resultant films were investigated in detail.

4.3 Materials and Methods

4.3.1 Materials

Worn T-shirts (95% cotton/5% elastane) were selected for this research. Sulfuric acid (95.0–98.0%) and sodium hydroxide (≥97.0%) were purchased from Sigma-Aldrich (Oakville, ON, Canada). Acetone (≥99.5%), lithium chloride (≥99.7%), N,N-dimethylacetamide (≥99%), and urea (≥99.6%) were purchased from Fisher Scientific (Ottawa, ON, Canada).

4.3.2 Preparation of RC Films

The dissolution and regeneration of waste cotton–elastane fabric were carried out according to our previous work with some modifications [11], and the dissolution conditions in different solvent systems are summarized in Table 4.1. Briefly, the textile was ground (KRUPS, Toronto, ON, Canada) until no fabric pieces could be observed, and the pre-treatment was required for the dissolution in H_2SO_4 and NaOH/urea aqueous solvents. A certain amount of fibers was dissolved with mechanical stirring (IKA Eurostar 60 digital mixer, Wilmington, NC, USA). The obtained solutions were degassed by centrifugation (Eppendorf centrifuge 5430, NRW, Hamburg, Germany) at 3000 rpm for 8 min and then spread on a glass plate and regenerated in coagulation baths. The cellulose films prepared from H_2SO_4 aqueous solvent, NaOH/urea aqueous solvent, and

LiCl/DMAc solvent were washed thoroughly with water; dried in air at room temperature; and coded as HRC, NRC, and DRC, respectively.

Table 4.1 Dissolution conditions of waste cotton-elastane fabric in three solvent systems.

Regenerated Film	**Pre-Treatment**	**Solvents**	**Dissolution Time**	**Dissolution Temperature (ºC)**	**Fabric Concentration (wt%)**
HRC	48 h in 20% (w/v) H_2SO_4	64% (w/v) H_2SO_4	45 min	0	3
NRC	60 h in 30% (w/v) H_2SO_4	7% NaOH/12% Urea	45 min	0	4
DRC	/	8% LiCl/92% DMAc	3-5 days	80	1

After regeneration and washing, the resultant wet RC films were padded with paper towels to remove excess water and sandwiched between two stainless steel plates for hot-pressing (Carver 3895, Wabash, IN, USA). All samples were first compressed at 90 ℃ and an applied pressure of about 1.1 MPa for 10 minutes to remove most water. Then, the films were compressed at various temperatures and pressures for 15 minutes. The hot-pressing conditions and sample codes are listed in Table 4.2.

Table 4.2. Hot-pressing conditions of RC films.

Sample codes	**Hot-press temperature (ºC)**	**Hot-press pressure (MPa)**
HRC1	120	4.45 MPa
HRC2	180	4.45 MPa
HRC3	120	44.5 MPa

HRC4	180	44.5 MPa
NRC1	120	4.45 MPa
NRC2	180	4.45 MPa
NRC3	120	44.5 MPa
NRC4	180	44.5 MPa
DRC1	120	4.45 MPa
DRC2	180	4.45 MPa
DRC3	120	44.5 MPa
DRC4	180	44.5 MPa

4.3.3 Mechanical Properties of RC Films

The mechanical properties of hot-pressed RC films were tested with an eXpert 7601 single-column testing machine (ADMET, USA) according to standard ASTM D882. Three strips with the dimension of 5 cm × 1 cm (length × width) were cut from each film sample, and the thickness was determined from SEM cross-section images. The testing speed was 5 mm/min with an initial grip separation distance of 20 mm. All hot-pressed films were stored at 25 °C and 50% RH for at least 2 days before the test.

According to the mechanical properties, the RC films hot-pressed at lower pressure (4.45 MPa) and different temperatures (HRC1, HRC2, NRC1, NRC2, DRC1, and DRC2) were selected for the following tests to study the effect of hot-pressing temperature.

4.3.4 Structure of RC Films

The FT-IR spectra of RC films (HRC1, HRC2, NRC1, NRC2, DRC1, and DRC2) were obtained using an FT-IR spectrometer (Cary 630, Agilent Technology, ON, Canada). The spectra were collected as the average of 72 scans with a resolution of 2 cm^{-1} from 650-4000 cm^{-1} at 25 °C, using the empty accessory as blank. Their morphology was observed by using a Hitachi TM1000 SEM (NJ, USA) at an acceleration voltage of 4 kV. The films were sputtered with 4 nm gold-platinum using a Leica EM ACE200 low vacuum coater (ON, Canada) before observation and photographing.

4.3.5 WVP and Thermal Stability of RC Films

A gravimetric method was used to evaluate the WVP of hot-pressed films (HRC1, HRC2, NRC1, NRC2, DRC1, and DRC2) according to ASTM E96-92 standard [18]. The films were sealed on a glass jar containing anhydrous calcium chloride with grease. Afterward, the jars were placed in a desiccator containing distilled water and the weights of the jars were measured periodically at 21 ºC. The WVP of the films was determined using Equation (1) [18]:

$$WVP = \frac{\Delta m \times k}{A \times \Delta T \times \Delta P} \tag{1}$$

where Δm is the change in the weight of the jar (g), k is the film thickness (m), A is the exposed area of the film (m^2), ΔT is the time, and ΔP is the partial pressure difference existing between the two sides of the film (Pa).The thermogravimetric analysis (TGA) of the RC films (HRC1, HRC2, NRC1, NRC2, DRC1, and DRC2) was performed with a thermogravimetric analyzer Q500 (TA instruments, DE) at a heating rate of 10 ºC/min in nitrogen (40 ml/min) from 50 to 600 ºC [19]. Thermograms of samples were collected, and the OriginPro software was used for calculating the percentage of weight loss.

4.3.6 Statistical Analysis

The experiments were carried out in triplicate and presented as the mean ± standard deviation. Statistical evaluation was applied with analysis of variance (ANOVA) followed by multiple comparison tests using Duncan’s multiple range test, and significant differences within samples were identified at $p < 0.05$. All the analyses were carried out through SPSS statistical software (IBM, NY, USA).

4.4 Results and Discussion

4.4.1 Mechanical Properties of Hot-Pressed Films

Mechanical properties of RC films are shown in Figure 4.1. It was clear that the hot-pressed RC films had much higher tensile strength and Young’s modulus than the air-dried films, which might be attributed to the enhancement of interaction between cellulose and elastane and the effective reduction of free volume through hot-pressing [12, 20]. Especially, the RC films prepared from LiCl/DMAc solvent system displayed the best tensile strength and elongation at break, followed by HRC films and NRC films. The highest tensile strength (231.04 ± 7.70 MPa) was achieved by DRC film hot-pressed at 44.5 MPa and 180 ℃, while the DRC film hot-pressed at 4.45 MPa and 120 ℃ showed the largest elongation at break (4.01 ± 0.64 %). These results were similar to our previous work in which the complete dissolution of elastane fibers provided DRC films with the uniform structure and best mechanical strength [17]. Only a slight increase in tensile strength was found in hot-pressed NRC films, and the values decreased considerably when high temperature and high pressure were applied. These results might be due to the existence of elastane fibers in NRC film causing uneven structure and easy failure during tensile tests [12]. Interestingly, the significant increases ($p < 0.05$) in tensile strength and Young's modulus were observed in HRC and DRC films when the hot-pressing temperature rose from 120 ℃ to 180 ℃, but the change in hot-pressing pressure did not cause any obvious improvement in three types of films. Therefore, only the RC films prepared at the hot-pressing pressure of 4.45 MPa were selected for the following tests to investigate the effect of treatment temperature. It was worth noting that the strengths of RC films presented in this work were comparable to those of hot-pressed cellulose films prepared from cotton linter pulp (188.7 MPa) [21], cellulose/multiwall carbon nanotube nanocomposites (156 MPa) [22], and softwood kraft pulp (104 MPa) [23].

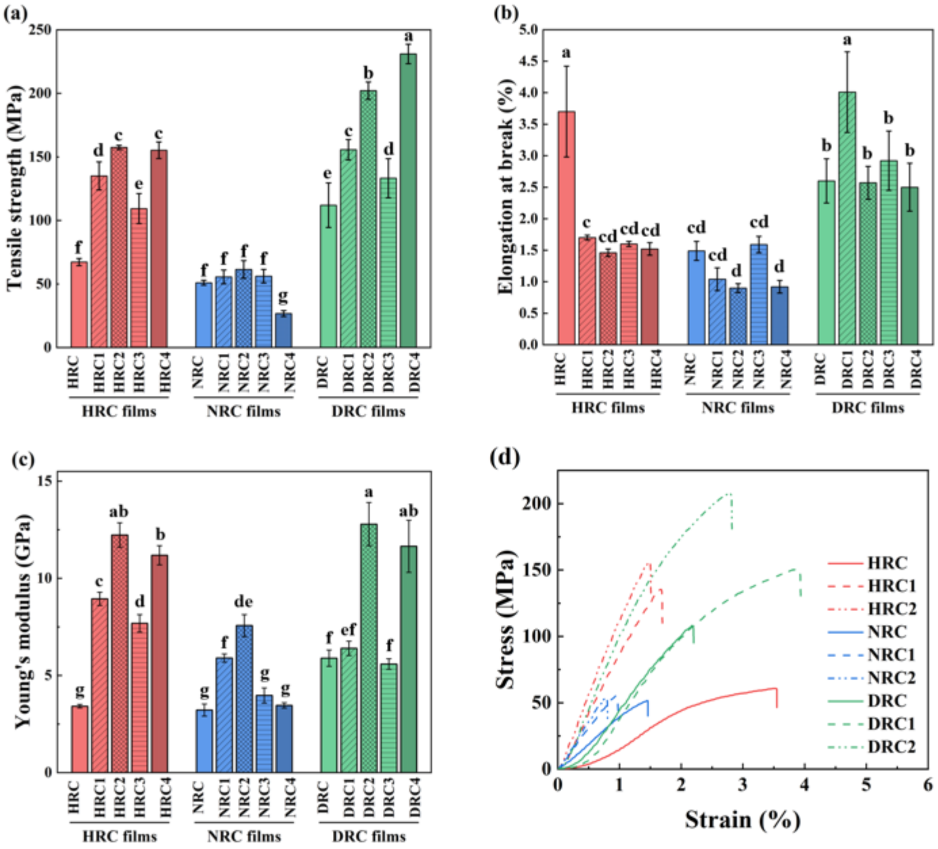

Figure 4.1 Mechanical properties of RC films prepared from three solvent systems by hot-pressing. Different letters on the tops of columns represented the significant differences ($p < 0.05$).

4.4.2 Structure of Hot-Pressed Films

To further study the effect of hot-pressing temperature on the structure of RC films, the SEM images of the surface and cross-section of the films hot-pressed at 120 °C and 180 °C were obtained. As shown in Figure 4.2, intact elastane fibers still existed in NRC films [17]. The fibers did not change after hot-pressing at 120 °C and slightly deformed at 180 °C, because elastane fiber has a melting point of 250 °C but noticeable thermal degradation was found at a temperature above 170 °C [24, 25]. A relatively smooth and uniform surface was observed for DRC films, which was attributed to the complete dissolution of both cotton and elastane fibers in the LiCl/DMAc solvent system. It was worth noting that the hot-pressed RC films exhibited a decreased thickness and smoother surface compared to the air-dried films, so a denser film structure could be expected. Moreover, the HRC and DRC films hot-pressed at 180 °C were thinner and smoother than the ones prepared at 120 °C. It might be due to the higher mobility of molecules at a higher temperature. It also explained the better mechanical strengths of HRC2, HRC4, DRC2, and DRC4. However, the cross-sections of NRC films were not uniform, and the intact elastane fibers prevented the formation of a compact film structure under hot-pressing.

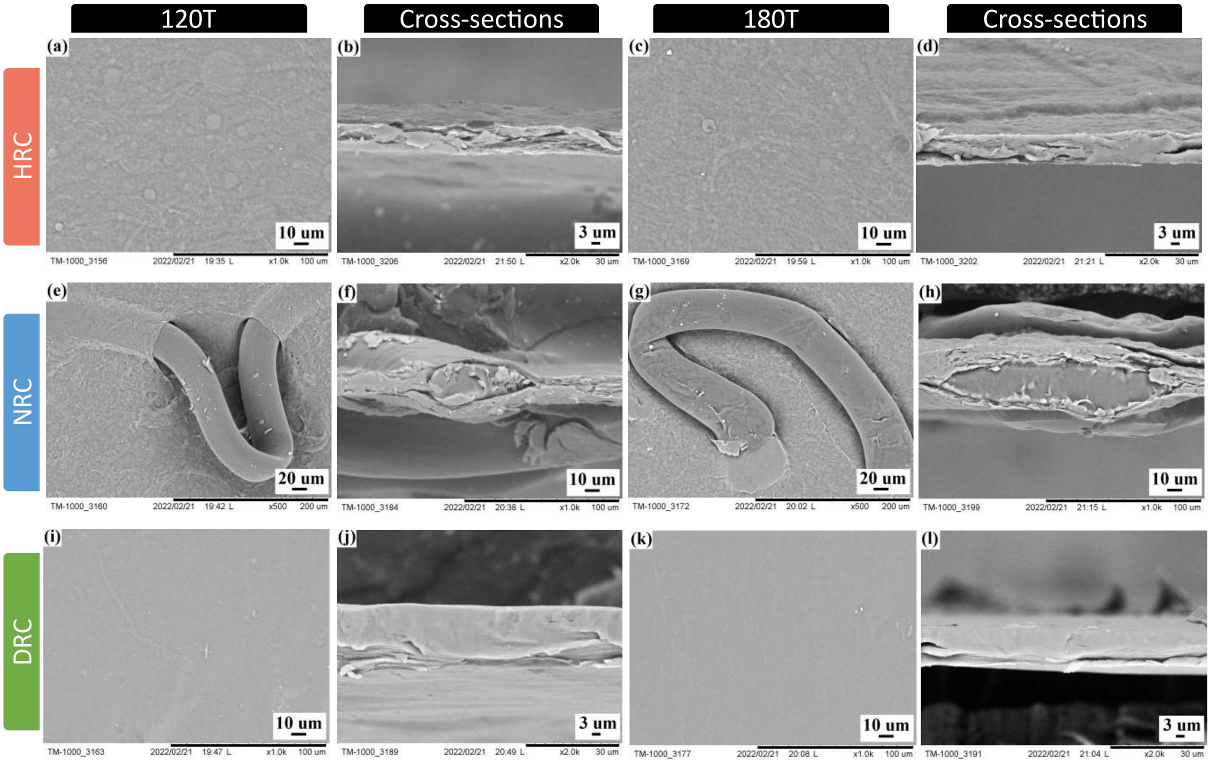

Figure 4.2 SEM images of RC film surfaces and cross-sections hot-pressed at 120 °C and 180 °C.

FT-IR spectra of waste textile, air-dried, and hot-pressed films are shown in Figure 4.3. Absorption peaks at 1431 cm^{-1}, 1364 cm^{-1}, 1333 cm^{-1}, 1314 cm^{-1}, and 895 cm^{-1} were observed in all the samples, representing -CH$_2$, -CH, and -OH bending, -CH$_2$ rocking vibration, and β-glycoside bonds of glucose ring, respectively [26, 27]. The broad peaks at 3275 cm^{-1} and 3340 cm^{-1} represented the intramolecular hydrogen bonds of cellulose I structure [11]. After dissolution and regeneration, the increase in band intensity at 895 cm^{-1} led to a decrease in the band intensity ratio of I$_{1430}$/I$_{900}$, which was due to the change in crystalline structure from cellulose I to cellulose II [28]. Characteristic peak at 1534 cm^{-1} representing the C-N stretching of amide II was only found in NRC films, which was from the well-retained elastane fibers [17]. However, the hot-pressing treatment did not lead to any obvious change in FTIR spectra. It suggested that no chemical reaction occurred during hot-pressing [29].

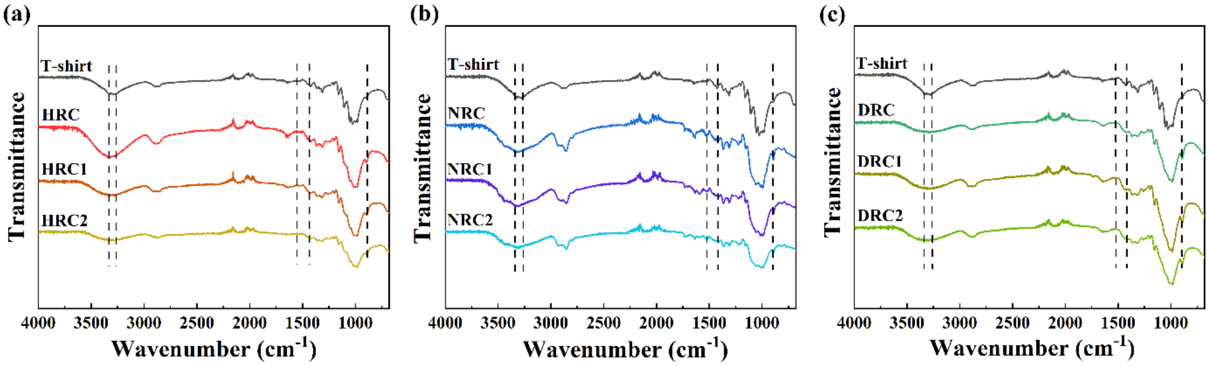

Figure 4.3 FT-IR spectra of waste textile air-dried and hot-pressed films.

4.4.3 WVP and Thermal Stability of Hot-Pressed RC Films

WVP values of air-dried and hot-pressed RC films are shown in Figure 4.4. For HRC and NRC films, the hot-pressing treatment obviously improved the water barrier property due to the compressed structure. Air-dried DRC films already had a low WVP value that was attributed to the well-dispersed elastane components in LiCl/DMAc solvent system among three types of films, so after hot-pressing the WVP values slightly decreased. The increase in hot-pressing temperature from 120 to 180 °C also caused a slight reduction of WVP values for HRC and DRC films. It suggested that the further reduced free volume had a significant effect on the mechanical strength but not on the water vapor barrier property because cellulose matrix is hydrophilic [12]. The lowest WVP value of $2.89 \pm 0.37 \times 10^{-8}$ g m^{-1} h^{-1} Pa^{-1} was found when DRC film was compressed at 180 °C, which was comparable to those of bleached kraft pulp films [30], corn starch/chitosan films [31], and cellulose/graphene oxide hot-pressed films [32].

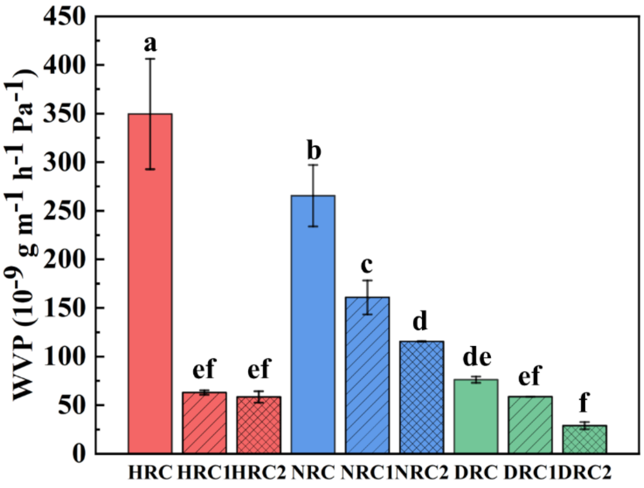

Figure 4.4 WVP values of air-dried and hot-pressed RC films. Different letters on the tops of columns represented the significant difference ($p<0.05$).

Figure 4.5 shows the TGA curves of hot-pressed RC films. All the films showed good stability from 50 ºC to 250 ºC with a small amount of weight loss due to dehydration [33]. Thermal decomposition of the RC films started at around 260-350 ºC and was associated with the degradation of cellulose and polyurethane molecules, where the thermal cleavage at the glycosidic linkages of cellulose and urethane hard segment happened [34, 35]. An additional weight loss occurred at around 350-520 ºC, representing the thermal degradation of cellulose inorganic ash [36]. The maximum decomposition temperatures for the primary and secondary weight losses of the RC films are listed in Table 4.3. It was worth noting that the thermal stability of RC films was independent of drying methods and hot-pressing temperature, which might be because of the lack of new chemical interactions during the physical treatment.

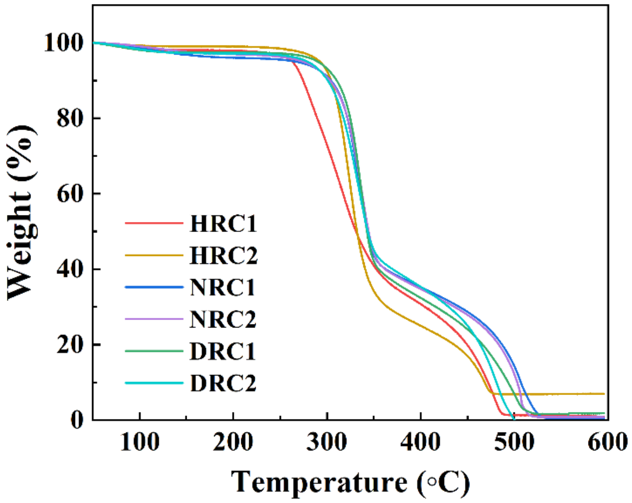

Figure 4.5 Thermogravimetric analysis of hot-pressed RC films.

Table 4.3 Maximum decomposition temperatures of hot-pressed RC films.

Samples	**Primary maximum decomposition temperature (ºC)**	**Secondary maximum decomposition temperature (ºC)**
HRC1	316.77	478.66
HRC2	324.50	469.31
NRC1	332.45	505.18
NRC2	337.67	504.94
DRC1	335.22	502.94
DRC2	333.10	480.50

4.5 Conclusion

In this study, the hot-pressing treatment was applied to quickly dry and compress the cellulose films dissolved and regenerated from H_2SO_4 aqueous solvent, NaOH/urea aqueous solvent, and LiCl/DMAc solvent. Compared to the air-dried RC films, the hot-pressed films exhibited significantly better mechanical strength and water vapor barrier property, as well as the well-retained thermal stability when the temperature was lower than 250 ºC. The results revealed that the tensile strength and Young's modulus of HRC and DRC films increased with the increase of hot-pressing temperature, while hot-pressing pressure showed no obvious effect on the strength of

RC films. The higher hot-pressing temperature also contributed to the reduction of WVP values, but the water vapor barrier property relied more on the hydrophobicity of the film matrix. Because of the full dissolution of cellulose and elastane fibers in LiCl/DMAc solvent system, the DRC films hot-pressed at 4.45 MPa and 180 °C showed the highest tensile strength (202.10 ± 6.82 MPa) and Young's modulus (12.79 ± 1.11 GPa), and lowest WVP value ($2.89 \pm 0.37 \times 10^{-8}$ g m^{-1} h^{-1} Pa^{-1}). Herein, the recycling of cotton/elastane textile wastes with solvent systems and hot-pressing exhibits great potential for fabricating packaging films with good performance.

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CHAPTER 5. GENERAL SUMMARY AND CONCLUSION

5.1 General Summary

The growing textile industry and the resultant textile wastes have raised concerns about environmental pollution. In the literature review, various methods used for recycling textile wastes in recent years have been summarized. Textile materials such as natural fibers, man-made fibers, and fiber blends can be recycled using mechanical, thermochemical, chemical, and enzymatic methods to leverage their values in the textile industry, environmental treatment, electrochemistry, engineering solutions, packaging materials, and micro-/nano-cellulose extraction. We aimed to use H_2SO_4 aqueous solution, NaOH/urea aqueous solution, and LiCl/DMAc solvent systems to recycle waste cotton fabrics containing elastane fibers. The results revealed that all three solvent systems could effectively dissolve the cellulose fibers, but different behaviors of elastane components were found in three solvents. Large intact elastane fibers were retained in NRC films and resulted in weaker mechanical properties than the other two films. The H_2SO_4 aqueous solvent could partially hydrolyze the elastane components, while LiCl/DMAc solvent was capable of completely dissolving the elastane fibers. Therefore, the DRC film exhibited a uniform structure, high transparency, high tensile strength (121.63 ± 6.16 MPa), low WVP ($1.03 \pm 0.53 \times 10^{-7}$ g m^{-1} h^{-1} Pa^{-1}), and a maximum decomposition temperature of 359.97 ºC. In addition, the regenerated cellulose films after hot-pressing treatment showed obviously higher mechanical strength and lower WVP values compared to the air-dried films. It was worth noting that the mechanical properties (tensile strength and Young's modulus) of hot-pressed films increased with the increase of hot-pressing temperature, while the higher hot-pressing pressure had no obvious impact on the films. Among all the films, DRC samples hot-pressed at 4.45 MPa and 180 ℃ displayed the highest tensile strength (202.10 ± 6.82 MPa), Young's modulus (12.79 ± 1.11 GPa), and lowest WVP ($2.89 \pm 0.37 \times 10^{-8}$ g m^{-1} h^{-1} Pa^{-1}).

5.2 Suggestions for Future Work

This work provides a promising strategy for directly recycling cotton textile wastes containing elastane fibers into regenerated cellulose composite films with high performance, which can be potentially utilized as packaging materials. Due to the existence of elastane residue, the effect on food quality should be investigated in the future. In addition, the elastane components are non-biodegradable, so it is necessary to further study the biodegradability of hot-pressed regenerated films and the amount and morphology of residues after degradation. It has been demonstrated that the three cellulose solvents we used are effective to recycle cotton textile wastes with low amount of elastane, but it is not clear if they are still useful when more or multi-types of synthetic fibers exist in the fabric. The hot-pressing treatment revealed that even a relatively low compressive pressure could largely improve the properties of regenerated cellulose films. It will be very interesting to apply this finding in the continuous production of cellulose films with high performance.

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