

Review

Green Chemistry Approach for Fabrication of Polymer Composites

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Abstract: Solvents are an inevitable part of industries. They are widely used in manufacturing and processing industries. Despite the numerous controlling measures taken, solvents contaminate our environment to a vast extent. Green and sustainable solvents have been a matter of growing interest within the research community over the past few years due to the increasing environmental concerns. Solvents are categorized as “green” based on their nonvolatility, nonflammability, availability, biodegradability and so on. The use of ionic liquids, super critical carbon dioxide and aqueous solvents for the fabrication of polymer composites is discussed in this review. The progress of utilizing solvent-free approaches for polymer composite preparation and efforts to produce new biobased solvents are also summarized.

Keywords: green solvents; ionic liquids; fused deposition modeling; polymers



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1. Introduction

Management of solvent wastes is a major problem within most industries. Almost all industries like textile, electronics, food, etc. are associated with large amounts of solvents, and their effective disposal is a matter of extensive research. The average use of solvents by various industrial fields is given in Figure 1 [1]. The continued use of organic solvents has raised environmental concerns. The chemical synthesis routes mostly involve hazardous solvents that can have deleterious effects on mankind. Large quantities of solvents are necessary for processing as well as purification. The annual industrial scale production of organic solvents has been estimated around 20 million metric tons [2]. Removal of solvents is usually associated with large costs and energy consumption. This can have serious implications when it comes to their end applications, especially when the biomedical field is concerned. The greener chemistry approach is gaining new insights in polymer science research. The concept of green chemistry was formulated by Paul Anastas and John Warner, with an overview of reducing chemical processes and products [3]. Absence of flammability, biodegradability, ease of availability, nontoxic nature, etc. are the prerequisites for a green solvent [4]. The commonly used green solvents in polymer chemistry include water, super critical carbon dioxide and ionic liquids [5]. Another approach includes solvent free conditions. Many industries are trying to switch to solvent free processes. Additive manufacturing techniques like fused deposition modeling is proven to be advantageous in this direction [6]. Water-based techniques are highly desirable. However, it is very difficult to dissolve most of the polymers in water. Supercritical fluids having both gas-

and liquid-like properties are also explored. The chemical regulations are growing more strict nowadays, especially in the UK which restricts many of the solvents commonly used for polymer dissolution in fields like paints, coatings, printing, adhesives etc. [7]. Hence, it is imperative that greener techniques and benign solvents are developed for polymer processing. This review highlights the importance of green solvents for the development of polymer composites.

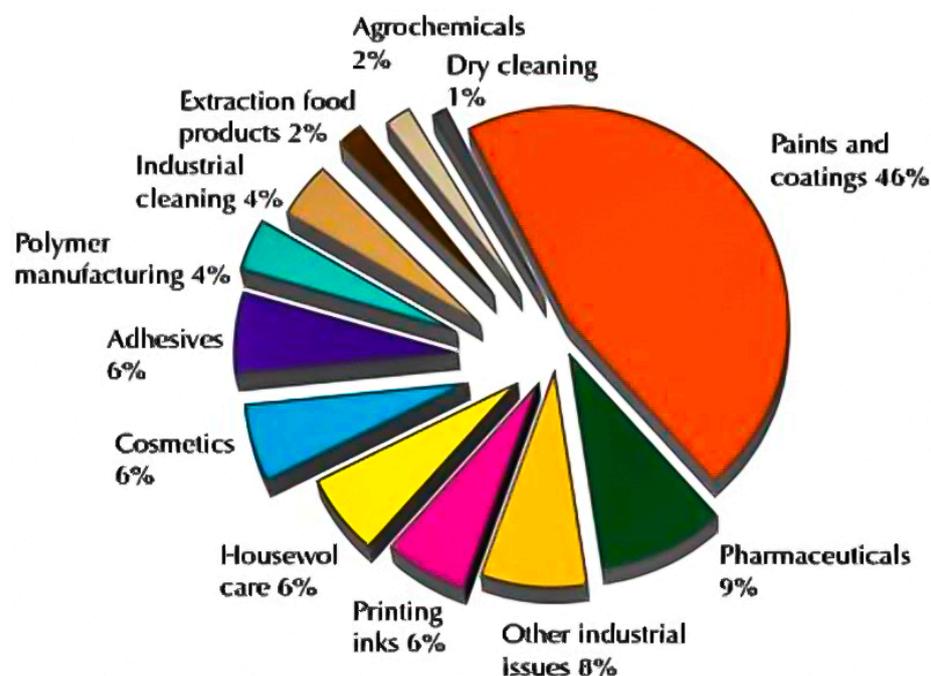


Figure 1. Average of use of solvents in different sectors. Reproduced with permission from [1].

2. Ionic Liquid Assisted Approach

Ionic liquids are made entirely of ions. For example, molten sodium chloride makes up an ionic liquid [8]. It should be noted that they can be liquid at temperatures as low as $-96\text{ }^{\circ}\text{C}$. The possibility of combining a number of anions and cations to prepare an ionic liquid makes this solvent very versatile [9]. Ionic liquids are more desirable than conventional solvents in industrially relevant applications mainly because they do not produce any volatile organic compounds. Chitosan films as vapor-sensitive luminescent sensors were prepared using chitosan, nanoclay and europium (III) complexes in the presence of carboxyl-functionalized ionic liquids (Figure 2) [10]. These free-standing luminescent films were prepared under aqueous conditions using ionic liquids in place of acetic acid to dissolve chitosan. The interesting feature of ionic liquids was that they boost the luminescence (quantum efficiency, 38%) of the film by lowering the proton strength on platelets and increasing the formation of europium (III) complexes with a high coordination number.

Soheilmoghaddam et al. reported the preparation of a biodegradable and cytocompatible polymer nanocomposite of cellulose and zeolite in the presence of the 1-ethyl-3-methylimidazolium chloride (EMIMCl) ionic liquid [11]. The EMIMCl ionic liquid is used to dissolve the cellulose polymer. Preparation of regenerated cellulose/sepiolite (RC/SEP) nanocomposite films using the ionic liquid 1-butyl-3-methylimidazolium chloride (BMIMCl) was reported. This ionic liquid was used as a solvent to dissolve cellulose and as a dispersion medium for sepiolite. In a similar approach, Caldas et al. reported the synthesis of poly (methyl methacrylate)-based nanocomposites where the graphene nanoplatelets were dispersed in the presence of imidazolium-, pyridinium-, and vinylpyridinium-based ionic liquids [12]. These composites demonstrated improved electrical conductivity and excellent microwave broadband absorption properties in the X-band

(8.2–12.4 GHz) frequency region, which is due to homogeneous dispersion of graphene nanoplatelets within the thermoplastic polymer matrix.

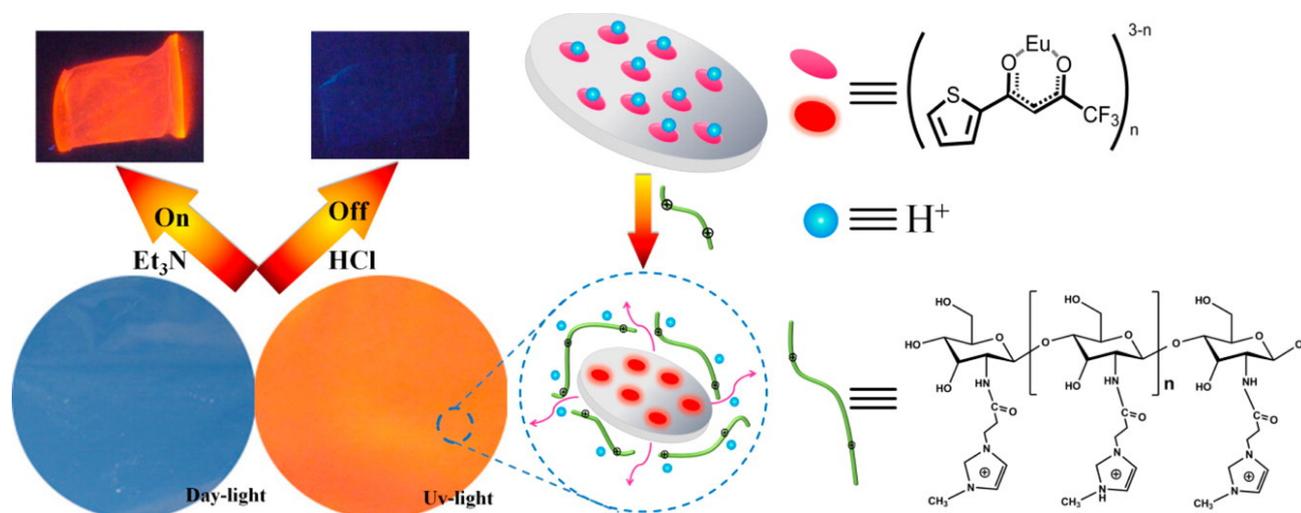


Figure 2. Schematic of the vapor-sensitive luminescent sensors based on chitosan, nanoclay, europium (III) complexes and carboxyl-functionalized ionic liquids. Reproduced with permission from [10].

Ionic liquids are immobilized by an inorganic or polymer matrix to form ionogel or ion gel. Their applications range from solid electrolytes to drug release to catalysis [13]. They are explored as temperature-resistant electrolyte membranes in electrochemistry devices [14]. Ionogels based on microcellulose and various methyl phosphonate ionic liquids were used to fabricate flexible transistors on papers [15]. As a potential substitute to liquid electrolytes being used in ionic gadgets, the development of ionogel membranes is the need of the hour. Hussan et al. reported the preparation of a transparent ionogel composed of poly (methyl methacrylate) and the ionic liquid 1-butyl-1-methylpyrrolidinium bis (trifluoromethyl sulfonyl imide) [16]. The addition of the ionic liquid to the polymer improved the thermal stability, ionic conductivity, luminescence intensity and amorphous nature.

Chitin, the second most abundant polymer on Earth, is a highly sought biopolymer because of its biocompatibility and availability. However, it is not soluble in most of the solvents, which limits its applications. There has been a growing interest in IL-based approaches for chitin dissolution and processing [17]. Very recently, Wang et al. described the synthesis of an epoxy nanocomposite containing chitin nanowhiskers, which was dispersed using the ionic liquid 1-Ethyl-3-methylimidazolium acetate [18]. Ionic liquid facilitates the dispersion of chitin nanowhiskers as nanofillers in the epoxy matrix and promotes the cross-linking with epoxy to obtain a transparent texture. Addition of chitin nanowhiskers to the polymer matrix improves the mechanical properties of polymer nanocomposites. Ionic-liquid-assisted synthesis of polyaniline/carbon nanotube hybrids through promoting the polymerization of aniline and dispersion of carbon nanotubes was reported [19]. These hybrid nanocomposites loaded into epoxy coatings impart the anti-corrosion properties. Zhao et al. described the homogenous dispersion of ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate functionalized graphene oxides in the epoxy matrix which enhanced the tribological properties [20]. Addition of low quantities of GO-IL was effective in reducing the wear and friction of epoxy under all lubrication conditions. Under harsh lubrication conditions, the formation of nanostructured tribofilm on the steel surface was evidenced.

Polymer electrolytes in the presence of ionic liquids is more advantageous to unstable and flammable liquid electrolytes used in Li-ion batteries. Blensdorf et al. reported the synthesis of hybrid composite polymer electrolytes employing ionic liquids, 1-butyl-3-methylimidazolium and 1-ethyl-3-methylimidazolium, poly (ethylene glycols) and silica nanoparticles [21]. Moreover, ionic liquids play a major role in improving the conductivity

and transference number of the composites. For instance, a hybrid polymer nanocomposite containing 55 wt.% of 1-ethyl-3-methylimidazolium and 300 MW PEG displayed conductivity of $1.24 \times 10^{-3} \text{ S cm}^{-1}$. Fabrication of a poly ortho aminophenol (POAP)/1-methyl-3-methylimidazolium bromide (MB) electrode for supercapacitor applications was reported [22]. The capacitance and power characteristic of the composite electrode was increased by the introduction of ionic liquid MB, which also increased electrode cyclability. Moreover, the ionic liquid imparted more active sites in the composite electrode for faradic reaction, and as a result, specific capacitance was increased than in pure POAP. Synthesis of biopolymer composites in the presence of ionic liquids was also reported. Marisol et al. described the preparation of polymer nanocomposites using the castor oil polyurethane foam and ionic liquids 1-Butyl-3-methylimidazolium chloride, 1-Butyl-3-methylimidazolium tetrafluoroborate and 1-(2-hydroxyethyl)-3-methyl imidazolium glycinate [23]. These biopolymer composites can be utilized for CO₂ capture while the fluorinated and amine groups of ionic liquids influence the selectivity of CO₂/CH₄. Recently, Chao et al. described that a polyethylene glycol diacrylate (PEGDA)-based electrolyte along with an ionic liquid directs the electrodeposition of silver nanofilaments from silver salt and subsequent dissolution [24]. Kinetics of silver nanofilaments formation and dissolution is influenced by the addition of an ionic liquid, especially an ionic liquid of >10 wt.% which limits the process.

Synthesis of ionic electroactive polymer composites using poly (vinylidene fluoride) (PVDF) and ionic liquids such as 1-Butyl-3-methylimidazolium chloride and 2-hydroxyethyltrimethylammonium dihydrogenphosphate by solvent casting method was reported [25]. These ionic liquids promoted the electrical conductivity, thermal stability and also degree of crystallinity of the polymer in polar β -phase. Due to good cytocompatibility and C2C12 cell proliferation, these polymer composites can be widely exploited for muscle tissue engineering applications. A similar study reported the preparation of ionic liquid-polymer composites made up of poly (vinylidene fluoride) and ionic liquid, 1-butyl-3-methylimidazolium tetrachloroferrate for the development of printable humidity sensors (Figure 3) [26]. Porosity of the composites increased with the increase in ionic liquid, and optimal surface was achieved with the addition of 20 wt.% ionic liquid to the polymer. The response of the humidity sensor was validated for its performance from 35 to 90%. The sensitivity of the developed sensor was found to increase with an increase in IL content. The incorporation of IL into the polymer increases the overall electrical conductivity, and the polymer crystallinity was induced especially at β -phase due to strong ion-dipole interactions.

Recently, the design of stronger chitin fibers as a polymer composite by blending chitin fibers and poly (lactic acid) using a wet-jet spinning method, in the presence of ionic liquid 1-ethyl-3-methylimidazolium acetate as a solvent, was developed [27]. Maximum plasticity and Young's modulus of the polymer blends was about 8.8% and ~6 GPa respectively. Moreover, a 1.5 times increase in tensile strength was observed with the polymer blend when compared to neat chitin. Zhao et al. reported the design and development of a flexible humidity sensor employing the hydrophobic ionic liquid and hydrophobic polymer for applications in human respiratory monitoring and noncontact switches [27]. In this study, the humidity-sensitive polymer composite made up of poly (vinylidene fluoride-co-hexafluoropropylene) and (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide), which exhibited linear response with good sensitivity. The design of the fibrous membrane-based humidity sensor displayed fast response and detected up to a 120 Hz humidity change because of its high surface area.

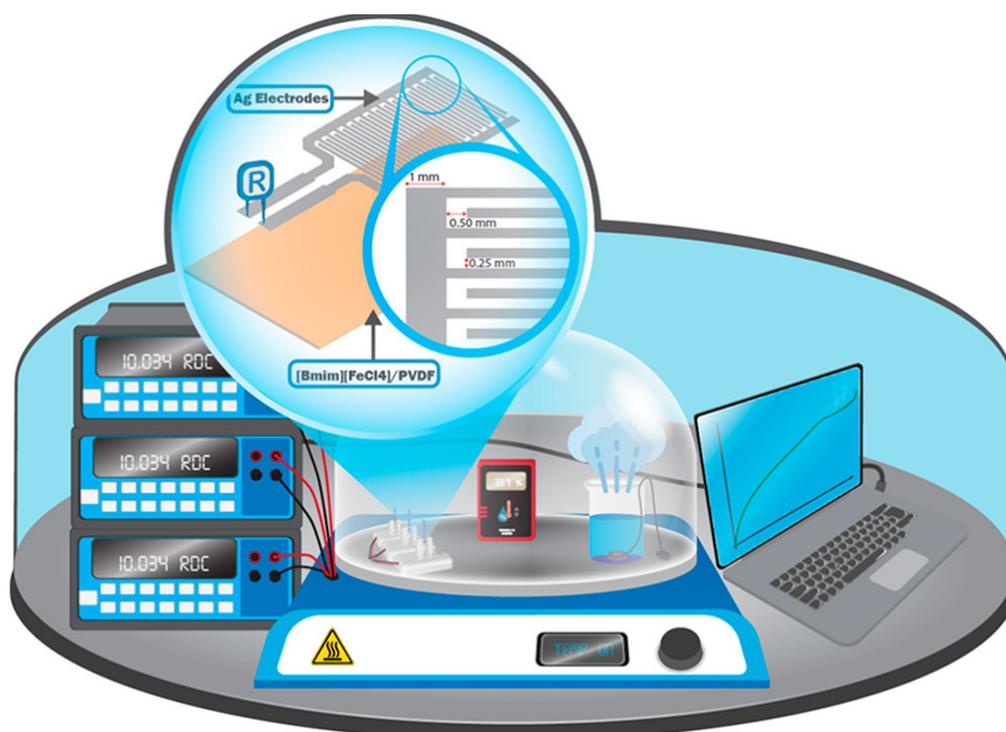


Figure 3. Schematic of the humidity sensor based on ionic liquid (poly (vinylidene fluoride)) composites. Reproduced with permission from [26].

3. Supercritical Carbon Dioxide Assisted Approach

Carbon dioxide is an attractive solvent for several industrial and chemical applications mainly because of its easy availability and inexpensive nature [28]. Conventional methods for synthesis of poly (N-isopropylacrylamide)-ferrite nanocomposites (PNC) utilize toxic and volatile organic solvents, require high temperature and high-cost. Supercritical fluid technology has been developed which meets these limitations of conventional methods and is suitable for large scale production. Most importantly, super critical carbon dioxide (SC-CO₂) acts as an efficient medium and operates at low temperature and pressure, thus maintaining the product integrity. Bisht et al. reported the preparation of a biocompatible magnetic nanocomposite composed of poly(N-isopropylacrylamide) and ferrite using the supercritical carbon dioxide for targeted and controlled delivery of doxorubicin (DOX) for breast cancer [29]. Integration of silk and platinum (Pt) in the preparation of bio-nanocomposites using SC-CO₂ was established for the applications in wearable and medical devices as shown in Figure 4. Here, the SC-CO₂ promotes the process of electroless plating (catalyzation) of Pt on silk textiles. Importantly, these composites demonstrated corrosion resistance, and electrical conductivity that remained even after adhesion tests.

In another study, the use of SC-CO₂ for the synthesis of branched poly (lactic acid) surfactants from the cyclic esters (D, L-Lactide) with polyols (D-Sorbitol) as a co-initiator was reported. The role of SC-CO₂ was to achieve controlled polymerization and purification of surfactants. SC-CO₂ as a green solvent significantly reduced the reaction temperature, favored narrower polymer dispersion and reduced side products [31].

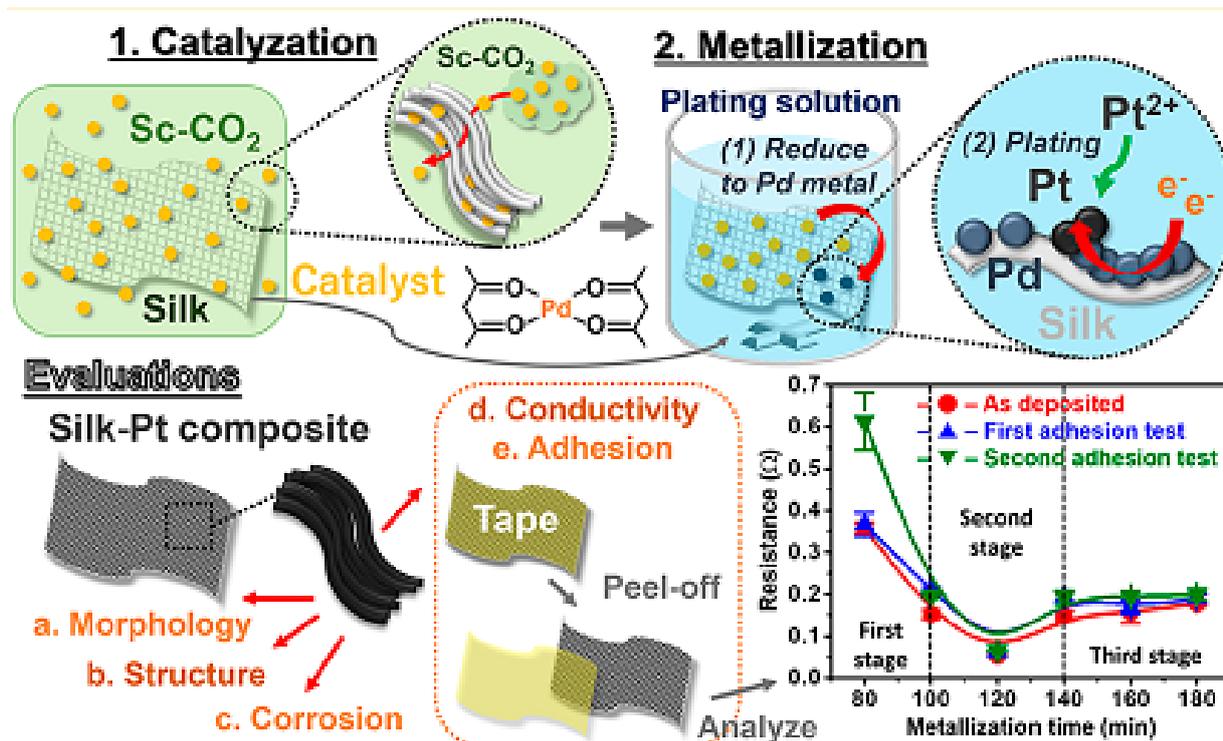


Figure 4. Outline of the development of biopolymer nanocomposite of silk and platinum using supercritical carbon dioxide. Reproduced with permission from [30].

High-performance electromagnetic interference (EMI) shielding materials based on metals or conductive polymer composites with electric fillers are used in the field of electronics, automobiles and packaging. As an alternative to metal-based shielding materials and other conductive polymer composites, Kuang et al. reported the synthesis of polymer-based nanocomposite foams made of poly (L-lactic acid) multiwalled carbon nanotubes using SC-CO₂ foaming and pressure induced flow (PIF) processing [32]. These lightweight, biodegradable polymer nanocomposites were found to be highly conductive and exhibited EMI shielding effectiveness of ~23 DB in the X-ray frequency region. The same research group reported the preparation of open-cellular porous poly (L-lactic acid) scaffolds by SC-CO₂ foaming for tissue engineering applications [33]. Physical foaming methods are not suitable for producing low-density and high-porosity PLLA scaffolds. To overcome these limitations, the integrated combination of PIF and SCC foaming assists the synthesis of PLLA scaffold with porosity of up to 92.5%. These high-strength PLLA scaffolds demonstrated remarkable cell adhesion and proliferation properties with mouse embryonic fibroblast cells. Introduction of disperse dyes in the polyester/co-polypropylene composite fibers using SCC was reported [34]. Unlike the conventional water dyeing process which is a burden in wastewater treatment, SCC based dyeing is a water-less process that is more economical and environmentally friendly. SC-CO₂ can also be used to prepare polymer composite membranes with high porosity for biological applications. In a recent example, a cellulose acetate (CA)-levan membrane was successfully prepared with interconnected pores with 9 to 13 μm size [35]. Mechanical resistance was increased upon the addition of levan, and cell adhesion was also increased from 8% to 30%.

Surface modification of nanomaterials is usually carried out in the presence of organic solvents, which are harmful to environment. Supercritical fluid-based technology can be readily applied for the synthesis or modification of polymer nanocomposites avoiding the use of toxic organic solvents. For instance, Matsuyama et al. reported that SC-CO₂ acts as a dispersion polymerization medium for the synthesis of poly (methyl methacrylate) (PMMA)-ZnO nanoparticle quantum dot (QD) composites as stable luminescent materials [36]. Surface modification of QDs with PMMA did not affect its intrinsic photolu-

minescence properties. Another example is SC-CO₂ mediated starch-modified magnetic (Fe₃O₄) nanoparticles for the removal of arsenic from ground water [37]. Starch-magnetic nanoparticles synthesised from SC-CO₂ modification process increased the adsorption capacity (*q_e*) relative to that of unmodified magnetic nanoparticles. These starch-Fe₃O₄ nanoparticles displayed As (III) adsorption of about 99% in 15 min from ground water.

Recently, large scale production of polylactic acid (PLA) scaffolds through the combined action of thermally induced phase separation and the SC-CO₂-based drying step was reported [38]. Conventional freeze-drying technology can be replaced by SC-CO₂ which demonstrates at least 50% reduction in environmental impact of overall process in life-cycle assessment methodology. Moreover, the production time was reduced from several days to hours to produce PLA scaffolds for bone tissue engineering applications. The extraction of cellulose nanofibers from plant biomass (total chlorine free bleached Kenaf fiber) using SC-CO₂ followed by mild acid hydrolysis is a benign step while the conventional extraction protocols involve the chlorine-based bleaching step which is not ecofriendly [39]. The cellulose nanofibers (0.3 wt.%) were processed through simple vacuum filtration and a hot-pressing step for the fabrication of cellulose nanopaper.

4. Aqueous Solvents

Jiang et al. prepared poly (tetrafluoroethylene)/graphene nanocomposites (PTFE/GNs) by utilizing an electrostatic self-assembly method [40]. The PTFE/GN nanocomposites were fabricated by the mixing of negatively charged GO and positively charged PTFE particles in the water. Then, reduction using hydriodic acid, cold briquetting, and hot sintering steps was carried out. The PTFE/GN nanocomposites having enhanced dispersion uniformity, notable electrical behavior, improved mechanical strength, and excellent compressive strength were formed by combining the latex technology and self-assembly method. This environmentally friendly strategy has eliminated the use of toxic organic reagents and difficult chemical functionalization and hence throws light on the synthesis of graphene-based polymer composites having high performance for a wide range of applications. Goncalves et al. reported the synthesis of water-based piezoresistive polyvinyl alcohol-carbon nanotubes (PVA-MWCNT) polymer composites [41]. Ultrapure water was used as the solvent to synthesize the PVA-MWCNT polymer composites for developing piezoresistive sensors having applications as medical devices and automotive components. The significance of the study lies in the use of green solvent water instead of the frequently used toxic solvents like chloroform, dimethylformamide, and toluene.

Yu et al. created a 4-dodecylbenzene sulfonic acid-doped polyaniline/Fe₃O₄ composite honeycomb structure film via a water-assisted self-assembly process. In the suitable composition of PANI-DBSA/Fe₃O₄ film, the superparamagnetic property was observed [42]. These 3D macroporous structures containing magnetic inorganic compounds and conducting polymers have applications as electronic-magnetic materials. Li et al. manufactured CsPbBr₃/SiO₂ nanocomposites via an in situ method using tetraethyl orthosilicate (TEOS) as silicon precursor and ethanol/water system as the solvent [43]. The nanocomposites synthesized via a one-pot and ethanol/water-assisted synthesis have displayed improved optical properties and stability as compared to that of neat CsPbBr₃ nanoparticles. The green ethanol-water system was useful to produce SiO₂ nanoparticles and phase transformation. The highly luminescent nanocrystals formed in this work using SiO₂ nanoparticles as a barrier layer have better environmental stability. Rousseaux et al. fabricated polypropylene (PP)/clay nanocomposites having excellent rheological, thermal, and mechanical characteristics through a water-assisted extrusion method [44]. The fabrication of PP-based nanocomposites with better clay delamination was done by the dilution into neat PP of PP-g-MA-based masterbatches formed with Cloisite 30B organoclay via a water-assisted process with high-shear rates. Because of the use of water in this process, an aqueous suspension of Cloisite 30B organoclay was formed, and hence the clay dispersion was raised during the melt blending. In addition, the usage of water resulted in nice

bonding between organoclay surfactant and PP-g-MA by acid-catalyzed esterification and MA hydrolysis.

5. Solvent Free Processing

Ryder et al. synthesized polymer metal composites using FDM (fused deposition modeling), and the physical and mechanical properties of the composites were tested [45]. The usage of FDM for the preparation of acrylonitrile butadiene styrene—stainless steel (ABS-SS) composites have resulted in improved mechanical properties of the materials with better functionality. The uniform dispersion of the particles was confirmed using SEM and MDSC scans. Up to a 15 wt.% of metal particle concentration, the glassy behavior of the polymer matrix was improved and a further increase in concentration has resulted in defects due to the metal additives, and the mechanical properties were adversely affected. The study concludes that the synthesis of polymer metal composites without a decrease in the mechanical properties is possible and new functionalities like magnetic properties can also be added to the material. Dickson et al. studied the characteristics of continuous carbon-, glass-, and Kevlar-fiber-reinforced composites synthesized using the FDM technique [46]. A Markforged Mark One 3D printing system was used for the manufacturing of nylon composites. It was clear from the results that the fibers produced using carbon fiber exhibited better mechanical characteristics which have shown 6.3 times higher tensile strength compared to the nonreinforced nylon polymer. With an increase in the volume fraction of carbon and glass fibers, the mechanical properties were affected because of the increase in the level of air voids. In addition, the results showed that at an 18% fiber content, the maximum tensile strength was exhibited by the glass specimen and the further increase in strength with fiber content was lesser. The synthesis of graphene-polymer composites using solvent-free powder mixing and in situ polymerization of a low viscosity oligomer resin was conducted by Noh et al. [47]. Using the solvent-free process, polymerized cyclic butylene terephthalate (pCBT) composites containing up to 20 wt.% graphene particles were produced maintaining high dispersion. In the composites, graphene nanoplatelets (C GNP), graphene oxide (GO), and GO reduced by phenylhydrazine (CCG-P) were used as the fillers. The study proved that the GO and CCG-P composites had better dispersion compared to that of C GNP composites as evident from SEM images (Figure 5). The most uniform dispersion was found in the CCG-P composites.

Fabrication of polymer composites using solvent-free melting processes has also been reported. In the studies of Yu et al., high-conductivity polymer composites were prepared by a one-step solvent-free melting process, based on powder mixing and in situ polymerization (Figure 6) [48]. The uniform dispersion of the graphene nanoplatelet (GNP) fillers in the composite films was confirmed by a 3D nondestructive X-ray microcomputed tomography (micro-CT) analysis technique which can be used for analyzing the internal structures of composite films. The conductive behavior of the prepared composite films was highly dependent on the GNP filler dispersion. This study provides a promising platform for the fabrication of low-cost conductive polymer films.

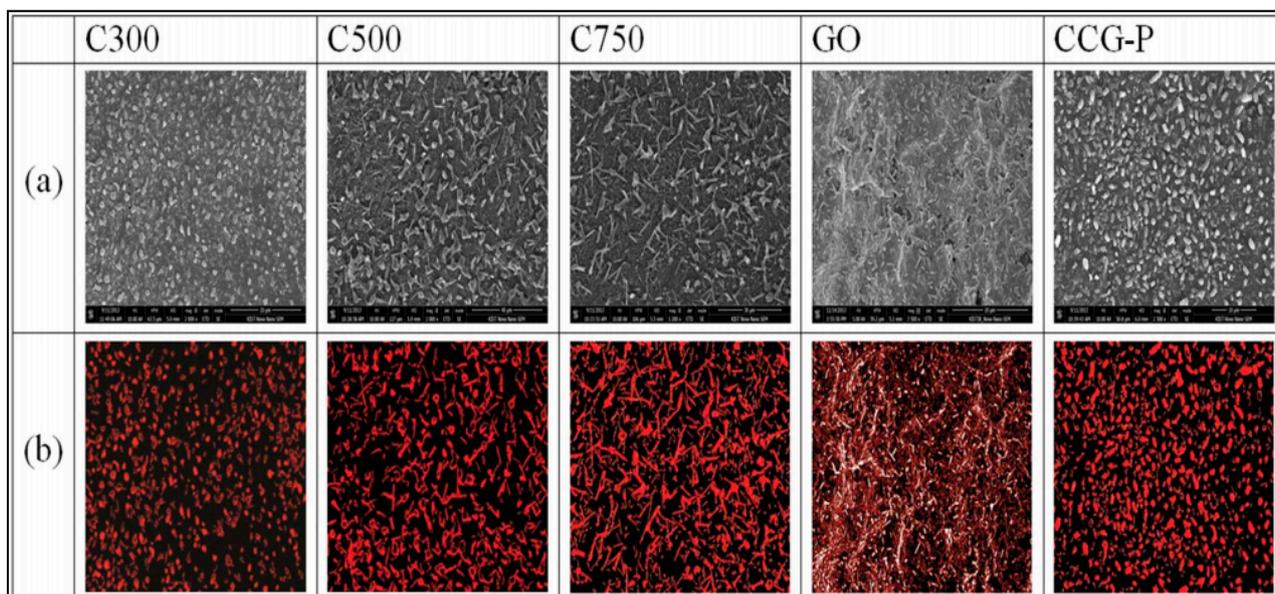


Figure 5. (a) SEM images, (b) digitally processed SEM images of the distance between fillers of C GNP filled (C300, C500 and C750), GO filled, and CCG-P filled pCBT composites. Reproduced with permission from [47].

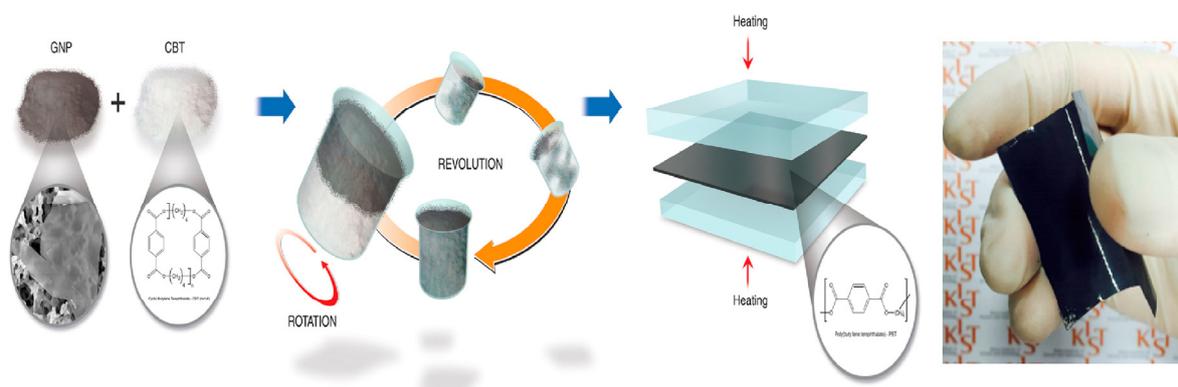


Figure 6. Schematic of solvent-free one-step synthesis based on powder mixing and in situ polymerization for composite film filled with highly disperse GNP fillers. Reproduced with permission from [48].

Tan et al. developed solvent-free porous composite scaffolds having applications in tissue engineering (TE) using rapid prototyping (RP) techniques [49]. The polyetheretherketone (PEEK)-hydroxyapatite (HA) biocomposite blends were made using a selective laser sintering (SLS) rapid prototyping system. The microstructure of the prepared three-dimensional TE scaffolds can be controlled using the SLS process parameters like scan speed, laser power, and part bed temperature. In addition, different amounts of hydroxyapatite can be incorporated into the polymer blends, and it can be used as tissue engineering scaffolds, especially as bone scaffolds. The computational design and fabrication of polycaprolactone (PCL) scaffolds were carried out by Williams et al. using selective laser sintering [50]. The mechanical characteristics, microstructure, tissue in-growth, and biological properties of the PCL scaffolds were analyzed in the study. The PCL scaffolds prepared using SLS have shown suitable mechanical properties as required for their bone tissue engineering applications. The in vivo studies have proven the ability of these PCL scaffolds to enhance the tissue in-growth which can be utilized in bone and cartilage tissue engineering applications. Yuan et al. prepared multiwalled carbon nanotubes/polymer composites using the SLS technique [51]. The study has shown that laser-sintered composites (s-CNT/PA12 and s-CNT/PU) are electrically conductive at less than 1 wt.% concentration of CNTs whereas the thermal conductivity was deleteriously af-

ected by the inevitable pores. These conductive polymer composites can have applications in various fields like automobile, aerospace and electronic packaging, etc. Badalov et al. proposed a new method for fabricating thin-film composite membranes by using interfacial polymerization and ink-jet printing techniques [52]. The synthesized composites formed by the incorporation of fluorinated diamine into m-phenylenediamine-based polyamide have resulted in membranes with better salt rejection due to an increase in selective layer hydrophobicity. The incorporation of the fluorinated monomer provides improved ion separation properties to the membrane. The usage of other functional monomers in the inkjet PAF methods is a future aspect of the study. The composite membranes prepared by this technique can be used for water treatment and desalination purposes.

Our group recently reported the fabrication of a polycaprolactone scaffold using fused deposition modeling without the use of any solvent. The polymer surface was modified by plasma polymerization after which gold nanoparticles were incorporated into the PCL surface using a surface immobilization technique [53]. The PCL scaffolds exhibited enhanced mechanical properties because of interface properties and uniform dispersion of gold nanoparticles (Au-PCL). The combination of fused deposition method and plasma technology resulted in the successful fabrication of 3D printed PCL scaffolds having sufficient biomechanical properties to be used in biomedical applications as seen from the nanoindentation studies. The plasma modified scaffolds containing gold nanoparticles (Au-PCL) showed greater proliferation of HFF2 cells than amine modified PCL (A-PCL) and neat PCL as seen in Figure 7. Thus, this study clearly shows that FDM is a potential method that can be used for fabricating tissue engineered scaffolds for biomedical applications.

Eng et al. developed polymer composites reinforced with oriented nanoclay through a 3D stereolithography (SL) technique [54]. The exfoliation of montmorillonite nanoclays, the homogeneous dispersion of nanoclays into the photopolymer by mixing, the orientation of nanoclays in layers by a bottom-up SL, and the immobilization of nanoclays by photopolymerization upon UV exposure were carried out. The tensile stress and Young's modulus in the X-Y plane of the polymer composites were improved, and the elongation was enhanced by more than 100% at 3wt.% clay concentration. Bustillos et al. has made use of the stereolithography 3D printing technique in order to generate photosensitive polymer-based boron nitride nanoplatelets (PSP/BNNP) composites [55]. The compressive yield strength of 1 wt.% BNNP was increased by 23.8% more than that of 0.5 wt.% BNNP, and hence the potential of using BNNP as the reinforcement agent in SLA 3D printed scaffolds was proved.

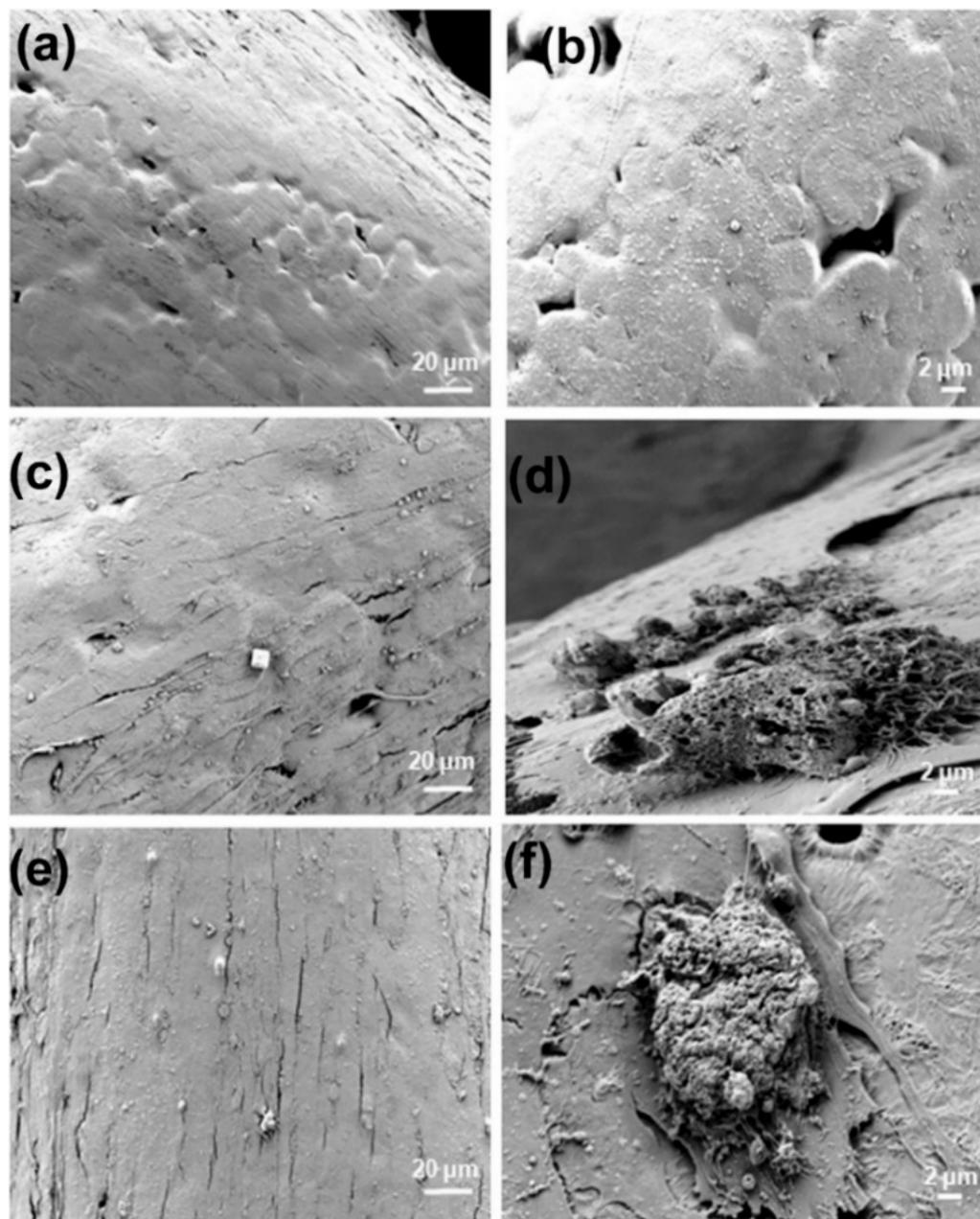


Figure 7. Evaluation of cell attachment and cell morphology on 3D printed scaffolds. SEM images of HFF2 cells attachment and spreading on unmodified PCL scaffolds (a,b), A-PCL scaffolds (c,d) and Au-PCL scaffolds (e,f). Reproduced with permission from [53].

6. Miscellaneous Green Solvents and Future Perspectives

Today, green chemistry and green technology is at the helm of the chemical industry. In 2015, the United Nations put forth its development plan for transforming our world: the 2030 agenda for sustainable development that addresses a wide array of issues, many of which emphasize the need for green chemistry and sustainable engineering [56]. The prime focus is to reduce our dependence on fossil fuels to produce chemicals such as monomers and solvents and replace them with sustainable biobased feedstocks. It also encompasses the manufacture, design and use of environmentally benign chemical processes that prevent environmental pollution, produce less hazardous waste and reduce human health risks. Agricultural products such as sugarcane, corn and maize were the first generation of biomass feedstocks, but their use to produce biosolvents remains contentious due to the rising concerns over food security [57]. The second-generation biomass feedstocks rely on

agricultural residues such as rice husks, orange peels and mainly lignocellulosic biomass to produce renewable solvents. However, the downstream processing of lignocellulosic biomass to sustainable solvents is a more energy- and cost-intensive process which hinders its commercial production and use [58,59].

Starch and cellulose are the major components of biomass which are composed of glucose units linked by glycosidic bonds containing α -1,4 and β -1,4 connections in starch and cellulose respectively [60,61]. The hydrolysis of cellulose and starch can be performed enzymatically or chemically to produce glucose [62,63]. Subsequent chemical transformations of glucose can provide a wide range of value-added chemical products, many of which may be used as green solvents for the fabrication of polymer nanocomposite. For instance, bioethanol can be produced from any biomass containing sugar molecules such as sugar beet, sugarcane, corn, sweet sorghum, rice straw and algae, etc. Generally, this process can be divided into three different steps: preparation of the fermentable sugar-containing solution; fermentation of this solution to produce bioethanol; and lastly, recovering and concentrating the bioethanol by distillation and dehydration process [64]. Bioethanol is generally used as an additive in fuel but could also replace conventional ethanol as a sustainable alternative with low toxicity [65]. Glycerol is another viscous liquid that is produced on an industrial scale from vegetable oils. Recently, the production of glycerol has been strongly accelerated due to a rapid increase in biodiesel production. As glycerol is the main by-product during the biodiesel production, its utilization in chemical processes is highly desirable in order to promote its commercial uses [66]. Glycerol appears to be a promising green solvent for pharmaceutical applications because it is a cheap, nonflammable, renewable and biocompatible liquid [67].

γ -valerolactone (GVL) has received much attention as a renewable fuel, but it can also be used as a green solvent for various chemical processes. There are two main routes to synthesize GVL, one from cellulose via production of hydroxymethylfurfural to levulinic acid, or via furfural from hemicellulose. GVL is a stable, colorless water-soluble liquid with a boiling point of 207–208 °C [68,69]. It does not decompose at room temperature and has melting point of -31 °C [70,71]. These properties make it a promising green solvent which can replace many conventional dipolar aprotic solvents in industry and academia. 2-methyl tetrahydrofuran (2-MeTHF) is yet another renewable alternative to THF which is now mainly used as a biofuel. 2-MeTHF has a boiling point of 80.2 °C and a melting point of -136 °C which is close to that of THF (boiling point of 66 °C and melting point of -108.4 °C). In addition, 2-MeTHF has higher stability and lower water miscibility and volatility than THF which makes it the best substitute for THF in many industrial applications. Initial studies have shown 2-MeTHF has lower toxicity and has been approved for use in pharmaceutical chemical processes [72]. It is usually manufactured from biomass derived xylose and glucose via other feedstock intermediates such as furfural and levulinic acid. Acidic pathways from levulinic acid via an intermediate of GVL can also produce 2-MeTHF. This pathway gives the potential for a dual high value stream for both these bio renewable solvents.

Cyrene (dihydrolevoglucosenone or 6,8-dioxabicyclo [3.2.1] octanone) is a ketone functional biosolvent which is manufactured via a two-step process from cellulose [72]. Firstly, cellulose is converted to levoglucosenone (LGO) followed by its hydrogenation to form cyrene. Cyrene has the potential to replace many chemical processes that require nonrenewable dipolar aprotic solvents such as Dimethylformamide (DMF), N-Methylpyrrolidone (NMP), and Dimethylacetamide (DMAc). It is worth mentioning that cyrene also facilitates near-perfect conditions for dispersing graphene and improving graphene exfoliation when compared to NMP [73]. Hence, cyrene has huge prospects for fine tuning the dispersion of nanofillers while fabricating polymer nanocomposites with tailored mechanical properties. D-Limonene (1-methyl-4-(1-methyl phenyl) cyclohexene) is a colorless liquid aliphatic hydrocarbon solvent which belongs to the class of cyclic monoterpenes and is the major component present in the essential oil of citrus fruit peels [74]. It is usually used as a dietary supplement and is also a component of the aromatic scents due to its inherent fragrance

from orange. Due to its biorenewable nature and higher boiling point of 176 °C, it can be used potential replacement for conventional high boiling solvents used for the fabrication of polymer nanocomposites. D-limonene can also replace solvents like acetone, methyl ethyl ketone, toluene, glycol ether and numerous fluorinated and chlorinated solvents that are commonly used during the fabrication of polymer nanocomposites [75]. Some of the possible pathways to fabricate green solvents and other intermediates from plant biomass, vegetable oils and waste biomass is summarized in Figure 8 [2].

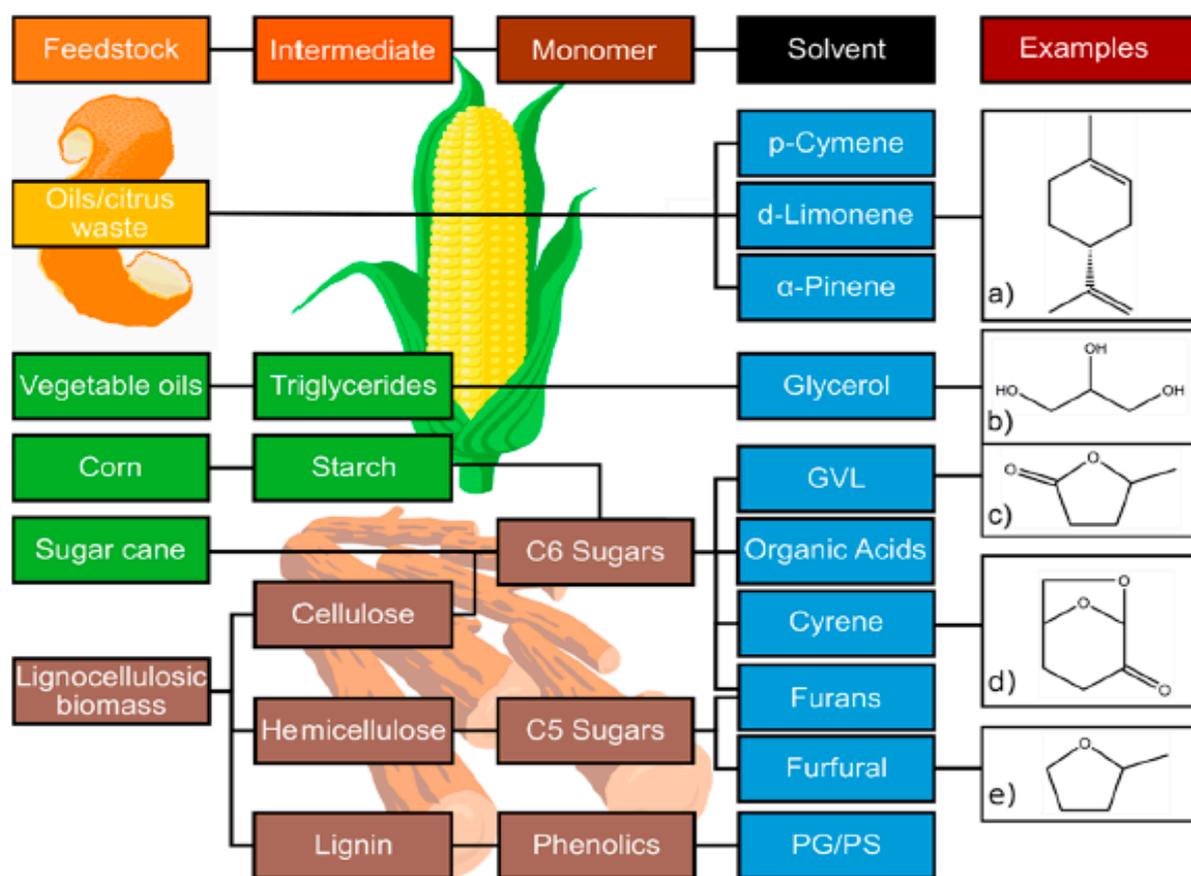


Figure 8. A number of sustainable solvents can be derived from plant biomass. While plant sugars and oils require less processing, lignocellulosic biomass can produce a broader range of solvents. Structural examples show (a) d-limonene, (b) glycerol, (c) γ -valerolactone, (d) cyrene, and (e) 2-MeTHF. Reproduced with permission from [2].

7. Conclusions

The utilization of biomass and agricultural waste for the fabrication of green solvents is the next paradigm shift in the chemical industry. The green solvents have many hurdles to large scale production such as feedstock diversity (composition variation from species-to-species, environmental factors and geographical locations), biomass transport and supply issues and, most importantly, the economic viability of the downstream processes. The solvents extracted from renewable and easily accessible resources are foreseen as future solvents for sustainable industrial applications. New technologies to bring down the production cost along with low energy consumption protocols needs to be devised to promote the industrial use of these green solvents on a commercial level.

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