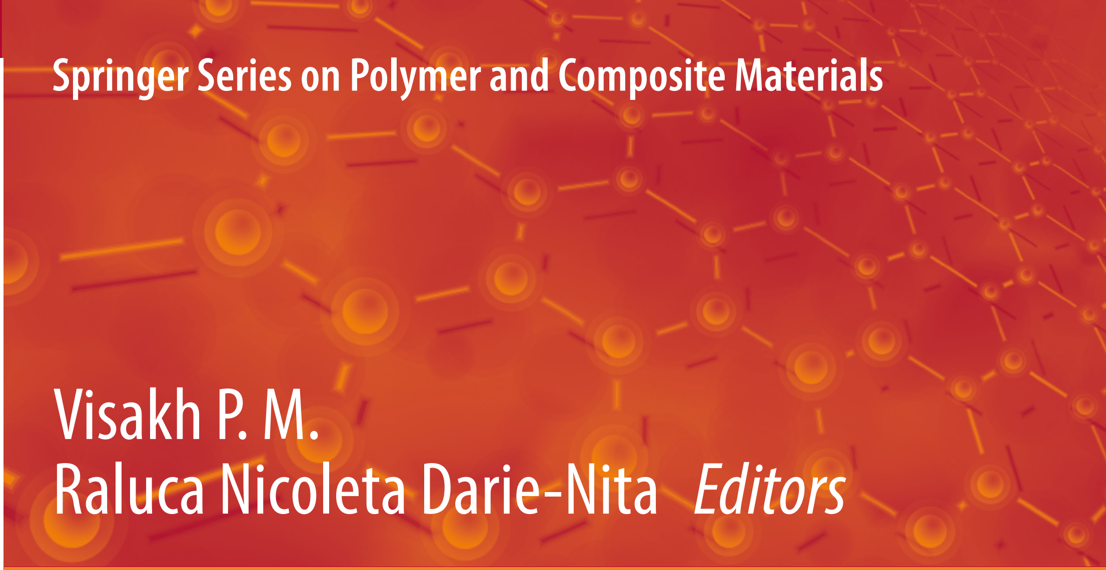

Springer Series on Polymer and Composite Materials

Visakh P. M.
Raluca Nicoleta Darie-Nita *Editors*

Polyvinylchloride-based Blends

Preparation, Characterization and Applications

Springer

Springer Series on Polymer and Composite Materials

Series Editor

Susheel Kalia, Army Cadet College Wing, Indian Military Academy, Dehradun, India

The “Springer Series on Polymer and Composite Materials” publishes monographs and edited works in the areas of Polymer Science and Composite Materials. These compound classes form the basis for the development of many new materials for various applications. The series covers biomaterials, nanomaterials, polymeric nanofibers, and electrospun materials, polymer hybrids, composite materials from macro- to nano-scale, and many more; from fundamentals, over the synthesis and development of the new materials, to their applications. The authored or edited books in this series address researchers and professionals, academic and industrial chemists involved in the areas of Polymer Science and the development of new Materials. They cover aspects such as the chemistry, physics, characterization, and material science of Polymers, and Polymer and Composite Materials. The books in this series can serve a growing demand for concise and comprehensive treatments of specific topics in this rapidly growing field. The series will be interesting for researchers working in this field and cover the latest advances in polymers and composite materials. Potential topics include, but are not limited to:

Fibers and Polymers:

- Lignocellulosic biomass and natural fibers
- Polymer nanofibers
- Polysaccharides and their derivatives
- Conducting polymers
- Surface functionalization of polymers
- Bio-inspired and stimuli-responsive polymers
- Shape-memory and self-healing polymers
- Hydrogels
- Rubber
- Polymeric foams
- Biodegradation and recycling of polymers

Bio- and Nano- Composites:-

- Fiber-reinforced composites including both long and short fibers
- Wood-based composites
- Polymer blends
- Hybrid materials (organic-inorganic)
- Nanocomposite hydrogels
- Mechanical behavior of composites
- The Interface and Interphase in polymer composites
- Biodegradation and recycling of polymer composites
- Applications of composite materials

More information about this series at http://www.springer.com/series/13173

Visakh P. M. · Raluca Nicoleta Darie-Nita
Editors

Polyvinylchloride-based Blends

Preparation, Characterization and Applications

Springer

Editors
Visakh P. M.
Faculty of Electronic Engineering,
Department of Physics Electronics
TUSUR University
Tomsk, Russia

Raluca Nicoleta Darie-Nita
Physical Chemistry of Polymers Department
“Petru Poni” Institute of Macromolecular
Chemistry
Iasi, Romania

ISSN 2364-1878 ISSN 2364-1886 (electronic)
Springer Series on Polymer and Composite Materials
ISBN 978-3-030-78454-6 ISBN 978-3-030-78455-3 (eBook)
https://doi.org/10.1007/978-3-030-78455-3

© Springer Nature Switzerland AG 2022
This work is subject to copyright. All rights are reserved by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed.
The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.
The publisher, the authors and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publisher nor the authors or the editors give a warranty, expressed or implied, with respect to the material contained herein or for any errors or omissions that may have been made. The publisher remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

This Springer imprint is published by the registered company Springer Nature Switzerland AG
The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

Preface

This book on **Polyvinylchloride (PVC)-based Blends: Preparation, Characterization and Applications** covers many of the recent research accomplishments in the area of PVC-based blends. Throughout the book, various topics are addressed, such as the current state of the art of PVC-based blends, new challenges, and opportunities. An emphasis is given to the types and sizes of components/fillers and optimum compositions of PVC blends, their processing and structure-properties relationships, modification/compatibilization methods, and possible applications.

The current book is a valuable reference source for university and college faculties, professionals, postdoctoral research fellows, senior graduate students, and researchers from R&D laboratories working in the area of PVC-based blends. Prominent researchers from industry, academia, and government/private research laboratories across the globe gave their contributions for the chapters within this book. Chapter 1 provides an introduction to the area of PVC blends, along with their compositions, preparation methods, applications, new challenges, and opportunities of this field. Chapter 2 offers a review on the structure–properties relationships for PVC. Characterization techniques of PVC/thermoplastic nano-blends are discussed in Chap. 3, while Chap. 4 deals with the applications of PVC/thermoplastic nano-, micro-, and macro-blends, including structural uses, packaging, military, and/or aerospace applications. The factors affecting the properties of PVC nano-, micro-, and macro-blends are covered in Chap. 5, with emphasis on mechanical properties, thermal stability, and electrical properties. Interface modifications and compatibilization of PVC nano-, micro-, and macro-blends are discussed in Chap. 6. Chapter 7 presents examples of bio-based plasticizers for PVC, authors covering several aspects such as recent progress in performance of PVC plasticizers as alternative to DEHP, petroleum-derived PVC plasticizers, green plasticizers for PVC, and PVC/compatible additives. Chapter 8 deals with PVC/polysaccharide blends, in particular describing the processing, compatibilization, and properties of PVC blends with several types of polysaccharides such as chitosan, cellulose, and starch. Chapter 9 of this book covers PVC membranes preparation, mathematical modeling, characterization, modification, and applications. Recent studies on bio-based PVC-related blends are summarized in the final chapter, the authors focusing on PVC bio-related nano-blends and bio-based blends of PVC with polyesters, polysaccharides, natural fillers, and poly (vinyl alcohol) (PVA). Finally, the editors would like to express their sincere gratitude to all the contributors of this book, who provided excellent commitment and support to the successful completion of this venture. We would like to thank all the reviewers who have taken their valuable time to make critical comments on each chapter. We also thank the publisher Springer for recognizing the demand for such a book and for realizing the increasing importance of the area of **Polyvinylchloride (PVC)-based Blends: Preparation, Characterization and Applications**.

Tomsk, Russia Dr. Visakh P. M.
Iasi, Romania Dr. Raluca Nicoleta Darie-Nita

Contents

About the Editors

Dr. Visakh P. M. (MSc, MPhil, PhD) is a prolific editor with more than 38 books already published. Now, he is working as Associate Professor in TUSUR University, Tomsk, Russia, since 2017. He did his postdoctoral research in Tomsk Polytechnic University, Tomsk, Russia (2014–2017). He obtained his PhD, MPhil, and MSc degrees from School of Chemical Sciences, Mahatma Gandhi University, Kottayam, Kerala, India. He edited 38 books from Scrivener (Wiley), Springer, Royal Society of Chemistry, Elsevier, and more than 25 books in press, (from Wiley, Springer, Royal Society of Chemistry, and Elsevier). He has been invited as a visiting researcher in Russia (2014 to present), Portugal (2013 and 2014), Czech Republic (2012 and 2013) Italy (2009 and 2012), Argentina (2010) Sweden (2010, 2011, and 2012), Switzerland (2010), Spain (2011 and 2012), Slovenia (2011), France (2011), Belgium (2012), and Austria (2012) for his research work. He has visited 12 countries; he has visited 15 universities in Europe. He has published 20 publications, 4 reviews, and more than 30 chapters. He has attended and presented more than 28 conferences, he has 1829 citations, and his h-index is 20. He acts as a guest editor for four international journals.

Dr. Raluca Nicoleta Darie-Nita (M.Sc., Ph.D.) is currently Senior Researcher at “Petru Poni” Institute of Macromolecular Chemistry, Iasi, Romania. She received her PhD in Chemistry (2009) and Postdoctoral degree in Biomaterials (2013) from the Romanian Academy. MSc in Organic Physical Chemistry (2001) and license in Chemistry and Physics (1999) were awarded by Faculty of Chemistry, “Al. I. Cuza” University of Iasi, Romania. She has over 20 years of experience in reactive processing (natural and synthetic, pure or recycled polymers), polymers compatibilization and chemical functionalization, physico-chemical characterization of polymers and composites, development of materials for food packaging and structural applications, and durability testing of plastic materials. She has published 66 papers (56 ISI), 1 book, 11 chapters, and has 3 patents (1 international). She is also a member of national and international grants (director for 2 national grants) and has attended over 150 conferences, giving oral and poster presentations. The high visibility of her scientific activity is reflected in more than 1100 citations, and H-index = 19 (Web of Science). She serves as guest editor for two international journals.

Chapter 1

Polyvinylchloride (PVC)-Based Blends: State of Art, New Challenges and Opportunities

P. M. Visakh and Raluca Nicoleta Darie-Nita

Abstract PVC is a versatile polymer used in a diversity of applications, function of its own, as well as its blending component's properties. Since the early 1930s, when commercial production of PVC started, it became a universal polymer due to its high performance and low cost, combined with the broad range of items that can be obtained by multiple processing techniques and variable parameters. For enhanced performances, PVC can be mixed with (bio)plasticizers, thermoplastics, rubbers, polysaccharides, minerals, natural fillers or other types of additives in order to improve PVC blends compatibility. PVC is found in various applications, such as building, packaging, automotive, military and aeronautic industries, medicine, ships construction, life rafts, garden hoses, swimming rings, footballs, toys, different cards and so on. PVC is also used in the preparation of membranes (e.g., for water treatment), owing to its good mechanical strength, abrasion resistance, chemical stabilization, thermal properties, low cost and corrosion resistance. Different factors affect the properties of PVC composites, such as processing techniques and parameters, the origin of the filler, its particle size and its aspect ratio, as well as its concentration and the homogeneity of its distribution in the polymer matrix. PVC bionanocomposites can be also produced by using nanoelements resulted from different renewable resources, e.g., cellulose, starch, chitin, inducing also PVC's biodegradability.

Keywords Polyvinylchloride · Structure · Properties · Compatibility · Applications · Blends · Plasticizers · Biocomposites

---

P. M. Visakh (✉)
Department of Physical Electronics, TUSUR University, Vershinina Street, 74, 634050 Tomsk, Russia

R. N. Darie-Nita
Physical Chemistry of Polymers Department, "Petru Poni" Institute of Macromolecular Chemistry, 41A Gr. Ghica Voda Alley, Iasi, Romania

V. P. M. and R. N. Darie-Nita (eds.), *Polyvinylchloride-based Blends*,
Springer Series on Polymer and Composite Materials,
https://doi.org/10.1007/978-3-030-78455-3_1

1.1 PVC: Structure and Properties Relationship

Commercial production of PVC has been initiated in Germany in the early 1930s, via emulsion polymerization. The heat stability and processing of PVC were firstly improved in 1932 when the plasticizers for PVC were discovered by Semon, the use of stabilizers being developed in 1930s [1].

Polymerization of vinyl chloride takes place by a free radical addition process, comprising four elementary reactions: initiation, propagation, chain transfer to monomer and bimolecular termination steps. PVC resin can be produced by the following mostly used methods: solution, bulk, emulsion and suspension polymerization.

PVC became a universal polymer due to its high performance and low cost, combined with the broad range of items that can be obtained from multiple processing techniques and parameters [2]. Flexible products like artificial leather can be realized from PVC obtained by emulsion polymerization. PVC powder can be combined with plasticizer resulting plastisol, which turn into plastigel by heating. The rheology of plastisol is highly influenced by the type, amount and molecular mass of emulsifier, particle size distribution and mean particle size of PVC [3, 4].

As neat PVC is a brittle and inflexible material with low commercial possibilities, and it requires additives for enhancing its applications. PVC degrades severely under high pressure and heat, at processing temperature of around 150 °C, hydrogen chloride being eliminated and color changes from white to yellow, then brown, turning finally black [5, 6].

Due to its excellent electrical properties, PVC is used in extensive electrical applications, especially for easily molded insulators. Structural features, chemical composition and the degree of molecular order are influencing the electrical properties of PVC. The dielectric properties of PVC offer a description of the hopping and rotating process of electrons involved in PVC and explain the phenomenon of dispersion related to its molecular configuration and ordering, as it influences the material’s conductivity [7].

PVC is used as an insulating material in many electrical appliances, wire and cables. Several tests are used to determine the effect of formulation variables on this insulating property, namely (1) resin conductivity (2) volume resistivity and (3) insulation resistance.

Optical properties are very important and refer to polarization, interface, antireflection and reflection properties [8]. Optical absorption studies provide details on the type of optical transitions, localized states and electronic band structures, making these materials striking for chemical sensors for detecting ionic species and display panels [9–12].

When evaluating thermal property of PVC, glass transition temperature T_g is very important, representing the temperature at which PVC changes from a hard or glassy state to a soft, rubbery state [13]. Characteristic thermal transitions can be recorded for PVC by differential scanning calorimetry (DSC). As formed in typical commercial process, PVC is very amorphous, with very low crystallinity degrees.

A crystalline PVC can be synthesized if the order is forced by polymerization conditions, such as extremely low reaction temperatures (−50 to −100 °C). When the polymer chain has no order or random order, it is called atactic, and PVC generally falls into this category. The melting point of fully syndiotactic PVC reported in the literature is about 400 °C [14], but such a perfectly syndiotactic polymer has not yet been synthesized.

PVC has a high chlorine content, but considering all the progress, there are several future demands for long-term development and research in the PVC industry, e.g., for the production of non-toxic plasticizer, without metal, non-toxic stabilizer, to overcome the possibility of replacing PVC with other polymers, e.g., by thermoplastic elastomers.

Due to its properties, PVC can be used in many applications, including building industry: cables ducting and conduits, guttering, potable and gravity pipes, window frames and doors, roller shutters, sheets and panels, reservoir linings, wall covering, flooring, sports stadium seats, etc. Identity cards, smart cards, credit cards and telephone cards are made up from PVC nowadays. Ships' construction, liferafts, garden hoses, swimming rings, footballs and toys are also made up of PVC.

1.2 Characterization Techniques of PVC/Thermoplastic Nanoblends

Adding a thermoplastic polymer, an elastomer or wood flour to the PVC together with nanofiller can significantly improve the properties of PVC. The addition of mineral nanofillers to macro-molecular organic mixtures, including PVC, led to polymeric nanocomposites characterized by low weight, low costs and improved properties. A second polymer can cover the surface of the nanofiller particles by increasing the interaction between the PVC-nanofiller [15, 16].

Various techniques can be used for a comprehensive assessment and characterization physico-chemical properties of PVC blends (i.e., stereochemistry, particle size distribution profile, surface charge, morphology and surface geometry, thermal and mechanical properties, etc.).

Several PVC/MMT and PVC/Na-MMT nanocomposites have been prepared by Madaleno et al. [17] via solution blending and solution blending coupled with melt compounding methodology. Morphological, thermal and mechanical characteristics of the formulated nanocomposites were evaluated. TGA analysis was used to follow the thermal behavior of pristine PVC and PVC-based nanocomposites and PVC/Na-MMT nanocomposites showing enhanced thermal stability over PVC/OMMT nanocomposites and pristine PVC.

Chipara et al. [18] prepared polyvinylchloride-single-walled-carbon nanotube composites (PVC-SWNTs) and investigated the thermal and spectroscopic properties of the formulated nanocomposites. DSC studies were performed to envisage the intermolecular interactions between PVC and nanofillers, and an increase in the glass transition temperature (T_g) of the polymeric matrix with the loading of PVC-SWNTs is being recorded.

A two-step reaction was employed by Mondragon et al. [19] to realize PVC/Poly (ε-caprolactone) (PCL)/organophilic montmorillonite (OMMT) and PVC/ Polylactide (PLA)/OMMT nanocomposites. The morphological properties of the nanocomposites were investigated by atomic force microscopy. Well-dispersed MMT particles within the corona or the polymeric matrix of all the nanocomposites containing 3% w/w clay were clearly revealed by AFM images. Clay dispersion and adhesion between MTT and polymeric matrix affected also the tensile strength and stiffness of the studied nanocomposites.

Transmission electron microscopy (TEM) coupled with bright field emission was employed for the morphology characterization of PVC/organically modified clays (nanofillers), viz. hectorite and bentonite nanocomposites prepared by Awad et al. [20]. TEM analysis demonstrated that hectorite and bentonite were in a well-dispersed nanosized state and by the content of plasticizer and dispersant affected the dispersion of nanofillers within the polymeric PVC matrix.

Gao et al. [21] investigated PVC nanocomposites intercalated with vinyl grafted polyhedral oligomeric silsesquioxanes containing methylacrylopropyl groups (PVC/V-POSS). The rheological behavior of nanocomposites was evaluated by torque and capillary rheometry, following the effect of blend, shear rate and shear stress on non-Newtonian index. Mathur et al. [22] performed the structural characterization of cadmium sulfide (CdS)-embedded polystyrene/polyvinylchloride (PS/PVC) nanocomposites (CdS-PS/PVC_{nc}) using small-angle X-ray scattering (SAXS) to evaluate the nano range dispersion in the composites. The SAXS analysis revealed that the CdS-PS/PVC_{nc} showed a higher scattering intensity when contrasted with their counterparts without CdS-dispersed specimens.

1.3 Applications of PVC/Thermoplastic Nano-, Micro- and Macro-Blends

PVC is widely used due to its good processability, low flammability and low cost. Its low thermal stability during melt processing is considered a drawback, but it can be ameliorated by incorporation of stabilizers and other processing additives. Various natural or synthetic inorganic nanofiller compounds have been added to PVC in order to improve their mechanical strength properties or to reduce cost.

Majority of micro-, nano- and macro-blends of PVC contain mainly polymethyl methacrylate (PMMA), polystyrene (PS), acrylonitrile butadiene styrene (ABS), ethylene–vinyl acetate (EVA) copolymer and other thermoplastic resins, together with plasticizers such as phthalates, citrates, adipates, nano-, micro- and macro-inorganic/organic fillers (e.g., calcium carbonate or kaolin), organic fillers (e.g., soy bean flour, wood flour (hard and soft), nutshell hull and flour, natural fibers) in concentration of 40–65 wt%.

PVC has gained more attention and influence in the industry and trading, due to its combination with other polymers and performance of nano materials, together with increasing demand of replacing wood, paper and metallic parts in several domains such as packaging, construction, military and aerospace applications. Various recipes of PVC were realized, improved and tested before their applications in packaging, parts of airplanes/helicopters, structural components of building construction, or in optical devices.

An increased attention was given to PVC nano blends to be used in packaging applications, i.e., PVC/montmorillonite materials [23, 24]. Among different polymers such as polyethylene (PE), polypropylene (PP), polyvinyl acetate (PVA), polyvinyl alcohol (PVOH), polyethylene terephthalate (PET), polyamide (PA), etc., PVC can be used as the main polymer in nanoblends and offer good properties of melt processing in various desired shapes of food packaging [25]. The influence of nanosized filler dopant salt, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) on the rheological properties of a blend electrolyte with ratio of 70 wt% of PMMA to 30 wt% of PVC was evaluated by Liew and Ramesh [26]. PVC nanoblends can be processed to realize specific materials with improved characteristics for military application by using inorganic fillers to increase electrical conductivity, improve resistance to heat or ultraviolet light, as well as reducing cost. For aerospace applications, PVC nanoblends can be used in: interior components, technical parts, structural elements as well as components for navigation, propulsion engineering and satellite technology.

Before PVC nanoblends are approved for aviation and aerospace applications, they must normally be tested for components and semi-finished products such as rods, sheets and tubes. PVC micro-blends can be used in specific materials that lead to innovations for fast, high-quality construction to improve aesthetics and increase work speed [27]. Although PVC has poor thermal stability, low impact strength and high melt viscosity of its applications in several industries were enlarged by several modifications of PVC [28], together with incorporation of plasticizers and elastomers [29].

PVC macro-blends are applicable to manufacture some interior or exterior parts of aircrafts, such as dashboard enclosures, radomes/nose cones, beverage carts, counter backsplashes, ceiling and wall panels and partitions, flooring, signage, video bezels, various seating parts, window reveals, shades and dust panes, components and box of sanitary kit, and equipment housings.

1.4 Factors Affecting the Properties of PVC Nano, Micro- and Macro-Blends

Amount influence of mineral fillers like alumina oxide, mica, calcium carbonate used on PVC/(α-MSAN)/(CPE) blend was studied by Zhang et al. [30]. With the increase in mineral amount, the tensile strength decreases due to a low interfacial interaction between the polymer matrix and filler. This was also confirmed by Bishay et al. [31] who used alumina filler for PVC blends and found that the increase in alumina powder (0–40 wt%) led to a decrease in elongation at break, due to the discontinuities in the structure of the PVC/Al blends. Jazi et al. [32] studied the effect of mass ratios of modified micro/nano-$CaCO_3$ particles in PVC/surface-modified $CaCO_3$ blends on the mechanical properties of the composites. Arayapranee et al. [33] studied the possibility of improving the mechanical properties of PVC blends by the combination of PVC with elastomers; therefore, they modified natural rubber by graft copolymerization with styrene and MMA using a batch emulsion polymerization process.

Ratman et al. [34] studied 50/50 PVC/ENR blends with different amounts of tribasic lead sulfate to see how the filler influenced the tensile strength of the blends, which were also irradiated using a 3.0 meV electron accelerator with doses from 0 to 200 kGy.

Ward et al. [35] used graphite and copper nanoparticles as fillers and showed that with the increase in filler concentration, the tensile strength values decrease. Yuan et al. [36] found that with the increase in CB loading, the tensile strength of the high-density polyethylene matrix also increases. When compared to the PVC/PEO/CB blends, the ones with PEGDE have lower tensile strength, because the addition of the PEGDE leads to a decrease in the stiffness of the blend caused by the replacement of interaction between the polymers with ones with the surface modifier.

As showed by Abu-Abdeen and Elamer [37] in their work, the increase in PVC amount from 0 to 80 phr in PVC-NBR vulcanized with 40 phr carbon black nanopowder nano blends leads to increase in elastic modulus (Young’s modulus), but the increase in PVC amount led to a decrease in abrasion resistance, elongation at break, the maximum degree of swelling and penetration rate. Another team [38] studied how using graphite filler in PVC/PEO blends affected the conductivity and mechanical properties of this blends. They found that with the addition of graphite to PVC/PEO blends, Young’s modulus values of PVC/PEO/graphite decrease and keep this tendency as the graphite loading increases, because of the deformation effect of graphite on the molecular chains in the polymer blend leading to reduced mobility.

PVC/$CaCO_3$ blends were studies by Guermazi et al. [39] which showed that with an increase in filler amount from 20 to 40% $CaCO_{3,}$ the elongation at break displays an obvious decrease. This can be attributed to a weaker interfacial adhesion between the polymer matrix and the filler because when the filler amount increases, the risk of formation of more aggregates is higher which are failure-initiation sites and lead to more stress concentration around dispersed $CaCO_3$ filler particles.

Esmizadeh et al. [40, 41] obtained PVC-NBR nanoblends by melt-mixing in a Brabender plastograph in which a self-cross-linking reaction occurs. The extent of cross-linking reaction increases with an increase in mixing parameters such as mixing and processing temperature, as well as on the rotor speed used. Bishay et al. [31] studied the influence of aluminum content on the hardness of PVC/aluminum (Al) micro-blends and found that with an increase in Al content from 0 to 40 wt%, the shore A hardness slightly decreased due to a weak interfacial adhesion between the polymer matrix and Al filler [42].

1.5 Interface Modification and Compatibilization of PVC Nano-, Micro- and Macro-Blends

Interface modification of polymers is a mechanical–physical–chemical process of realizing the compatibilization between two or more components in order to tailor the final material's properties for various practical applications like sensors, actuators and electrodes [43–45], nano- and ultrafiltration membranes [46, 47], advanced building materials with improved photo-aging and flame retardant properties [48], nanocomposites with antibacterial properties and other biocompatible materials with medical use [49–53], and even pyrotechnic signaling compositions [54, 55]. From the mechanical studies, it was observed that with increase to 15 wt% of EVA-g-MAH concentration, the PVC/PA11 blends achieve maximum values for tensile modulus, tensile strength, elongation at break and impact strength. Above 15 wt%, the EVA-g-MAH excess is immiscible with PA11, leading to a decrease in compatibilization and mechanical properties.

Niu and Li [56] studied the in situ compatibilization of PVC/polystyrene (PS) blends catalyzed by anhydrous aluminum chloride. They investigated the structure of PVC/PS blends by means of FTIR and the properties by means of mechanical tests, SEM and DSC analysis. Asadinezhad et al. [57] added a coating of polysaccharides on medical-grade PVC, evaluating the surface characteristics and the extent of bacterial adhesion. Surface chemistry is the main factor that determines most of the polymer surface properties. It basically refers to the molecular structure and organization on the surface that is also a measure of the tendency of the substance to undergo surface reactions. The formation of co-cross-linked product at the PVC/PE interface was confirmed to be very important for the final product properties. Xu and his team [58] studied the influence of NBR (content of acrylonitrile 33.5–36.5 wt%) on the properties of PVC/low-density polyethylene (LDPE) blends and also the synergism with cross-linking agent. Novel PVC/silica–lignin blends were synthesized and characterized by Klapiszewski et al. [59] by means of thermal analysis (TGA), morphology (optical microscopy and SEM) and mechanical properties. It is well known that the structure of blended materials determines their properties, especially such structural factors like bonding strength on the interface between the dispersed phase and polymer matrix, shape of dispersed phase inclusions and homogeneity of filler particle distribution in the polymer matrix.

Eastwood and Dadmun [60] studied multiblock or blocky distributed chlorinated polyethylene (bCPEs) ability to strengthen PVC/POE interface in comparison to that of randomly distributed chlorinated polyethylene (rCPE), by means of asymmetric double cantilever beam, peel test experiments, XRD and DSC analysis.

1.6 Biobased Plasticizers for PVC

Over 95% of all of the medical PVC is used to manufacture bags for storage of blood and blood components, endotracheal tubes, catheters, drains, connectors used in hemodialysis, hemofiltration, autotransfusion, surgery, anesthesia and intensive care [61]. The value of PVC for use in medical applications is given by its: flexibility; chemical stability and possibility of sterilization; low cost and availability; biocompatibility with the human body.

The literature reported that phthalates represent more than 85% of world plasticizers production, out of which 90% is annually used in PVC manufacturing [62]. They are used in amount of maxim 40% from the overall material. In addition, PVC materials containing DEHP represent a problem also from the perspective of environmental protection. They are slowly biodegraded in the environment, so it is impossible to be recycled, and during combustion of the PVC waste, dioxin is produced. However, eco-friendly bioremediation of phthalates from medical devices has been largely studied. Thereby, three mycelial fungi, *Aspergillus parasiticus*, *Fusarium subglutinans* and *Penicillium funiculosum,* were found able to completely consumed intact DEHP physically bound to blood storage bags made from PVC [63]. The increased interest in the development of biobased plasticizers for PVC is related to the plasticizers synthesized from: biorenewable plant oils (e.g., rice fatty acid, soybean oil [64], hydrogenated castor oil, camphor [65]), agricultural by-products (e.g., sugar cane [66], glucose [67]) and waste (e.g., cooking oil [68, 69]). The synergetic effect of epoxidized soybean oil (ESBO) on hydrogenated castor oil plasticizer was demonstrated by investigation the plasticizer migration, tensile properties and dynamic friction of plasticized PVC films. The main application of these materials is for the wire and cable manufacturing industry.

A series of bioplasticizers for PVC based on a renewable monomer derived from glucose, isosorbide diesters, with different alkyl chain length, namely isosorbide dibutyrate (SDB), isosorbide dihexanoate (SDH), isosorbide dioctanoate (SDO) and isosorbide didecanoate (SDD) have been successfully prepared by Yang et al. [70]. An epoxidized glycidyl ester of soybean oil fatty acids (EGESOFa) has been obtained by Chen et al. [71] as an efficient alternative plasticizer for manufacturing PVC products to satisfy the health, food safety and environmental demands. Li et al. [72] designed and produced PVC tissue mimicking material for needle insertion by adding mineral oil and micro-sized glass beads to the PVC polymer. They conducted a factorial design of experiment by changing three factors; the ratio of softener and PVC polymer solution, the mass fraction of glass beads and the mass fraction of the mineral oil.

1.7 PVC/Polysaccharides Blends

Cellulose, chitin/chitosan, starch and glycogen are several of the most popular polysaccharide materials used in blends with PVC.

Bigot et al. [73] grafted seaweed antibacterial polysaccharides onto PVC surfaces using an original click chemistry pathway. PVC isothiocyanate surfaces (PVC–NCS) were first prepared by nucleophilic substitution of the chloride groups by isothiocyanate groups.

Sobahi and his team [74] prepared carrier-mediated blends of chitosan with PVC using nanoparticles of dithizone and utilization of different solvents to optimize the homogeneous mixing of the blend components. The obtained blends were found to have reasonable extent of compatibility. Such compatibility depends mainly on the way how the components have been blended with each other. The polymer-supported dithizone was investigated toward its ability to be used for removal of some metal ions from their aqueous solutions.

Badr et al. [75] have utilized heparin-modified chitosan (H-chitosan) membrane to enhance biocompatibility of sodium selective membrane electrode based on the highly thrombogenic PVC. Xu et al. [76] used chitosan as interface self-reinforcing and antibacterial agent in modified PVC-based wood flour composites to improve the interface adhesion as well as endow a novel antibacterial function to wood flour (WF)/PVC composites. Chitosan (CS) was found as a novel coupling agent for PVC composites with wood flour (WF/PVC) that improved interfacial adhesion. Xu et al. in their study [77] aimed at investigating the effects of adding chitosan of varied addition amounts and particle sizes on thermal and rheological properties of PVC/WF composites. Antibacterial activity is another CS feature that has been observed [78]. Based on the results of FTIR, SEM and DMA analysis, the ability for interface self-reinforcement of CS has been revealed. Exposure of PVC/WF/CS composites to moisture for long term resulted in significant increase in water absorption. There has been sufficient antibacterial activity observed when adding the certain amount of CS to compound.

Djidjelli et al. [79] prepared composites using PVC as a polymer matrix and 10, 20, 30 wt% of WF as a filler. The obtained results indicate that the mechanical properties of the composite deteriorate when the content of wood flour increases. On the other hand, this filler content has little effect on thermal properties. The authors stated that the PVC/WF composite can be produced by conventional techniques; however, the wood flour content should not exceed 20%.

Due to the very high surface energy, nanotubes tend to aggregate and are difficult to disperse in the polymer matrix [80]. Ghasemi et al. [81] presented an analysis of the morphology and mechanical properties of PVC/WF/multiwall carbon nanotubes (MWCNTs) foams. The nanocomposites were prepared in an internal mixer and foamed using a batch process. Nanoparticles were functionalized by sodium hypochlorite solution, and foaming was carried out by using azodicarbonamide as a chemical blowing agent.

Matuana et al. [82] investigated aminosilane as adhesion promoter, improving significantly the tensile strength of the PVC/wood composites. Authors suggested that treated cellulosic fibers can react with PVC to form chemical bonds. Other treatments (dichlorodiethylsilane, phthalic anhydride and maleated polypropylene) were found to be ineffective, giving strengths similar to those of composites with untreated cellulosic fibers.

Xu et al. [83] studied the effect of adding CS to the PVC/WF blend to improved compatibility and thermal stability of material. The thermal degradation temperature of PVC/wood flour composites increased after adding CS.

1.8 Preparation of PVC Membranes, Characterization, Modification, Applications and Mathematical Model

PVC is used in the preparation of membranes, owing to its acceptable characteristics as good mechanical strength, abrasion resistance, chemical stabilization, thermal properties, low cost and corrosion resistance [84, 85].

PVC/polycarbonate (PC) blend ultrafiltration membranes for water treatment were prepared via NIPS method by Behboudi et al. [86]. The polymer solution was prepared from PEG, PVC and PC in NMP. The homogeneous solution was degassed overnight then cast onto a glass plate using an automatic casting knife.

Doubé and Walsh [87] studied the behavior of mixtures of PVC with solution chlorinated polyethylene as a function of temperature and investigated the thermally induced phase separation (TIPS) by optical, dynamic mechanical and electron microscope techniques. PVC membrane was prepared by TIPS through using the polymer solution in different weight ratios using tetrahydrofuran (THF) as a solvent.

Fang et al. [88] studied blending of PVC/poly(methyl methacrylate-g-polyethylene glycol methacrylate) membranes in water and ethanol immersion baths and observed that the hydrophilicity and antifouling properties of blended membranes were higher than that of neat PVC membrane. Blending of PVC with different percentage of polycarbonate produced high-performance ultrafiltration membrane, where rejection of Bovine serum albumin from synthetic solution was 98.9% using 50% of polycarbonate blending with PVC with high permeate flux. Using a combination of non-solvent induced phase separation (NIPS) and TIPS in PVC membrane preparation can produce ultrafiltration membranes with sponge-like/bi-continuous structures with 60% porosity and rejection of dextran solution more than 90%.

1.9 Biobased PVC-Related Blends

A key solution for decreasing the environmental pollution caused by disposal of PVC non-degradable waste is the use of biodegradable polymers, additives and their mixtures.

Hachemi et al. [89] realized new bioblends based on PVC and polylactic acid (PLA). These immiscible polymers were compatibilized in situ by using maleic anhydride (MAH), while dicumyl peroxide (DCP) was used as initiator to enhance the blends processability. TGA results showed that the incorporation of PLA in PVC matrix increased the thermal stability of the blends. Phase separation has disappeared in the presence of MAH, microscopic observations revealing uniformly dispersed PLA in the PVC matrix.

Different types of PVC nanocomposites containing metals or metal oxides were proposed [90], but efforts were also turned to find natural antibacterial materials that could be easily incorporated in PVC by common techniques [91]. The natural origin of the filler, its particle size and its aspect ratio, as well as its concentration and the homogeneity of its distribution in the polymer matrix are important factors affecting the properties of PVC biocomposites [92]. Compared with synthetic fillers, the natural reinforcements present some advantages such as natural alignment of the carbon–carbon bonds and also its significant strength, stiffness, low density, low cost and biodegradability [93].

PVC bionanocomposites can be also produced by using nanoelements resulted from different renewable resources, e.g., cellulose, starch, chitin [94]. Cellulose nanocrystals characterized by high aspect ratio and a large interface area were used as reinforcing materials in PVC matrix. Blending PVC with biodegradable cellulose derivative is intended also to thermally support the polymer during the molding process, as well as to enhance the biodegradability of PVC waste products. Biodegradable nanocomposites of PVC and nanocellulose whiskers (in content of 0.1%, 0.5%, 1%, 3%, 5%, 8%) isolated from rice straw were prepared by melt-mixing. PVC was used as an additive to crystalline polyhydroxybutyrate valerate (PHBV) to improve PHBV's mechanical and processing properties, depending on the hydroxyvalerate (HV) content [95]. Compared with PVC materials containing conventional plasticizers, the PVC/polycaprolactone (PCL) blends are tougher, more extensible, with improved softness, and higher resistance to extraction by oil and water [96, 97]. The glass transition temperature of compatible PCL/PVC blends was evaluated by Koleske and Lundberg from the dynamic mechanical tests (DMA) by means of a torsion pendulum [98]. Co-precipitation of cross-linked starch xanthate with PVC latex, co-concentration of a starch and PVC latex, and dry mixing of starch and PVC were used to incorporate three levels of DOP and different amounts of starch in PVC matrix [99].

The influence of starch incorporation into PVC plasticized with di(2-ethylhexyl) adipate (which is susceptible to fungal attack) was assessed by Rosa et al. [100]. Tensile strength at break and elongation at break reduced, while Young's modulus increased with raising the starch contents of the mixture, indicating that the incorporation of starch decreased the plasticized PVC/starch blend flexibility; therefore, a more rigid material resulted due to the formation of new intermolecular interactions probably owing to hydrogen bonds. PVC matrix is blended with natural fillers in order to produce composites with low cost, overall light-weight and good mechanical properties successfully used as construction materials or in the automotive and furniture industries. The natural fillers include wood fiber and lignin [101–103], as well as natural plant fibers such as jute, bamboo, rice straw and sisal [104].

1.10 Conclusions

PVC is widely used since its commercial production in 1930s due to its properties such as good mechanical strength, abrasion resistance, chemical stabilization, thermal properties, low cost and corrosion resistance. Neat PVC or combined with (bio) plasticizers, thermoplastics, rubbers, polysaccharides, minerals, natural fillers or other types of additives are found in various applications, such as building, packaging, automotive, military and aeronautic industries, medicine, ships construction, garden appliances, toys, cards, membranes (e.g., for water treatment). In order to realize performant products containing PVC, different factors should be taken into consideration, such as processing techniques and parameters, the origin of the filler, its particle size and its aspect ratio, as well as its concentration and the homogeneity of its distribution in the polymer matrix. PVC's biodegradability can be initiated by combining PVC with fillers from renewable sources.

References

1. Morawetz H (1982) History of polymer science and technology. Marcel Dekker, New York
2. Yarahmadi N, Jakubowicz I, Martinsson L (2003) PVC floorings as post consumer products for mechanical recycling and energy recovery. Polym Degrad Stab 79:439–448
3. Borroso EG, Duarte FM, Couto M, Maia JM (2008) A Rheological study of aging of emulsion and microsuspension based PVC plastisols. J Appl Polym Sci 109:664–673
4. Rasteiro MG, Tomás A, Ferreira L, Figuredo S (2009) PVC paste rheology: study of process dependencies. J Appl Polym Sci 112:2809–2821
5. Unar IN, Soomro SA, Aziz S (2010) Effect of various additives on the physical properties of polyvinylchloride resin. Pak J Anal Environ Chem 11:44–50
6. Elgozali A, Hassan M (2008) Effect of additives on the mechanical properties of polyvinylchloride. J Sci Technol 9:1–12
7. Bahgat AA, Sayyah SM, Shalabi HS (1998) Electrical properties of pure PVC, in science and technology of polymers and advanced materials (Prasad PN, Kandil SH, Kafafi ZH (eds)). Springer, Boston, New York, pp 421–428
8. Mohan KR, Achari VBS, Rao VVRN, Sharma AK (2011) Electrical and optical properties of (PEMA/PVC) polymer blend electrolyte doped with $NaClO_4$. Polym Testing 30:881–886
9. Hasan BA, Saeed MA, Hasan AA (2012) Optical properties of poly vinyl chloride PVC films irradiated with beta and gamma–rays. Brit J Sci 7:14–28

10. Aleshin AN, Mironkov NB, Suvorov AV, Conklin JA, Su TM, Kaner RB (1996) Transport properties of ion-implanted and chemically doped polyaniline films. Phys Rev B 54:11638–11643
11. Ogura K, Saino T, Nakayama M, Shiigi H (1997) The humidity dependence of the electrical conductivity of a soluble polyaniline–poly(vinyl alcohol) composite film. J Mater Chem 7:2363–2366
12. Devi CU, Sharma AK, Rao VVRN (2002) Electrical and optical properties of pure and silver nitrate-doped polyvinyl alcohol films. Mater Lett 56:167–174
13. Agarwal S, Sexena NS, Agrawal R, Saraswat VK (2013) study of mechanical properties of polyvinyl chloride (PVC) and polystyrene (PS) polymers and their blends. AIP Conf Proc 1536:777–778
14. Gouinlock EV (1975) The fusion of highly crystalline poly(vinyl chloride). J Polym Sci Part B Polym Phys 13:1533–1542
15. Hakkarainen M (2003) New PVC materials for medical applications the release profile of PVC/polycaprolactone-polycarbonate aged in aqueous environments. Polym Degrad Stab 80:451–458
16. Feldman D (2014) Poly(vinyl chloride) nanocomposites. J Macromol Sci Part A Pure Appl Chem 51(8):659–667
17. Madaleno L, Thomsen JS, Pinto JC (2010) Morphology, thermal and mechanical properties of PVC/MMT nanocomposites prepared by solution blending and solution blending + melt compounding. Compos Sci Technol **70**:804–814
18. Chipara M, Cruz J, Vega ER, Alarcon J, Mion T, Chipara DM, Ibrahim E, Tidrow SC, Hui D (2012) Polyvinylchloride-single-walled carbon nanotube composites: thermal and spectroscopic properties. J Nanomaterials 2012:435412
19. Mondragón M, Valdes SS, Espíndola MES, López JER (2011) Morphology, mechanical properties, and thermal stability of rigid PVC/clay nanocomposites. Polym Eng Sci 51:641–646
20. Awad WH, Beyer G, Benderly D, Ijdo WL, Songtipya P, Gasco MMJ, Manias E, Wilkie CA (2009) Material properties of nanoclay PVC composites. Polymer 50:1857–1867
21. Gao J, Du Y, Xing L (2011) Rheological behavior and mechanical properties of PVC/V-POSS nanocomposites. Adv Mater Res 217–218:555–558
22. Mathur V, Sharma K (2014) Small angle x-ray scattering analysis of PS/CdS, PVC/CdS & PMMA/CdS polymeric nanocomposites. e-J Surf Sci Nanotechnol 12:420–422
23. Wan CY, Qiao XY, Zhang Y (2003) Effect of different clay treatment on morphology and mechanical properties of PVC-clay nanocomposites. Polym Test 22:453–461
24. Chazeau L, Cavaille JY, Terech P (1999) Mechanical behaviour above Tg of a plasticised PVC reinforced with cellulose whiskers; a SANS structural study. Polymer 40:5333–5344
25. Marsh K, Bugusu B (2007) Food packaging—roles, materials, and environmental issues. J Food Sci 72(3):R39–R55
26. Thabet A, Mobarak YA, Bakry M (2011) A review of nano-fillers effects on industrial polymers and their characteristics. J Eng Sci 39(2):377–403
27. Ede AN, Ogundiran A (2014) Thermal behaviour and admissible compressive strength of expanded polystyrene wall panels of varying thickness. Curr Trends Technol Sci CTTS 3 (2):110–117
28. Siddiqui MN, Redhwi HH, Vakalopoulou E, Tsagkalias I, Ioannidou MD, Achilias DS (2015) Synthesis, characterization and reaction kinetics of PMMA/silver nanocomposites prepared via in situ radical polymerization. Eur Polym J 72:256–269
29. Abdelrazek EM, Elashmawi IS (2008) Characterization and physical properties of $CoCl_2$ filled polyethyl-methacrylate films. Polym Compos 29:1036–1043
30. Zhang Z, Zhang J, Zhu WQ (2018) Low-cost poly(vinyl chloride)/poly (-methylstyrene-acrylonitrile)/chlorinated polyethylene/mineral fillers composites with highly improved thermal conductivity I: mechanical and thermal performance. Polym Compos 39:553–559. https://doi.org/10.1002/pc.23968