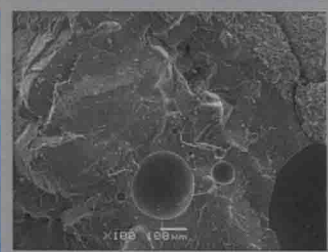


# Poly(Ethylene Terephthalate) Based Blends, Composites and Nanocomposites



Edited by  
Visakh P.M.  
Mong Liang



# POLY(ETHYLENE TEREPHTHALATE)BASED BLENDS, COMPOSITES AND NANOCOMPOSITES

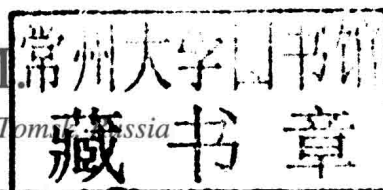
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The Boulevard, Langford Lane, Kidlington, Oxford, OX5 1GB, UK  
225 Wyman Street, Waltham, MA 02451, USA

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### British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library

### Library of Congress Cataloging-in-Publication Data

A catalog record for this book is available from the Library of Congress

ISBN: 978-0-323-31306-3

For information on all William Andrew publications  
visit our website at <http://store.elsevier.com/>

Typeset by Thomson Digital  
Printed and bound in the United States

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<a href="http://www.elsevier.com">www.elsevier.com</a> • <a href="http://www.bookaid.org">www.bookaid.org</a>		

Publisher: Matthew Deans  
Acquisitions Editor: David Jackson  
Editorial Project Manager: Peter Gane  
Production Project Manager: Lisa Jones  
Designer: Maria Ines Cruz

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TEREPHTHALATE)BASED  
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*Poly(Ethylene Terephthalate) Based Blends, Composites and Nanocomposites* summarizes many of the recent research accomplishments in the area of polyethylene terephthalate (PET)-based polymer blends, composites, and nanocomposites, such as, modification of polyethylene terephthalate; reinforcement of polyethylene terephthalate via addition of carbon-based materials; polyethylene terephthalate-based blends: thermoplastic and thermoset; polyethylene terephthalate-based blends: natural rubber and synthetic rubber; characterization of polyethylene terephthalate-based composites and nanocomposites; polyethylene terephthalate: copolyesters, composites, and renewable alternatives; molecular weight determination of polyethylene terephthalate; degradation kinetic parameter determination of blends containing polyethylene terephthalate (PET) and other polymers with nanomaterials; modification of polymer composites by polyethylene terephthalate waste; and highly functionalized polyethylene terephthalate for food packaging.

As the title indicates, the book emphasizes on the various aspects of PET-based blends, composites, and nanocomposites. This book is intended to serve as a “one-stop” reference resource for important research accomplishments in the area of PET nanocomposites, and will be a very 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 PET-based blends, composites, and nanocomposites. The various chapters in this book have been contributed by prominent researchers from industry, academia, and government/private research laboratories across the globe, and are an up-to-date record of the major findings and observations in the field of PET-based blends, composites, and nanocomposites.

The first chapter on PET-based blends, composites, and nanocomposites gives an overview of the state of the art, new challenges and opportunities of thermal stability-based studies and research, preparation, characterization, and applications of PET-based blends, composites, and nanocomposites and also future trends of PET-based nanocomposites.

The second chapter provides a good structure of the modification of PET-based blends, composites, and nanocomposites. This chapter explains different modification methods of PET-based blends, composites, and nanocomposites such as radio-frequency plasma,

ultraviolet (UV) technique, protein immobilization on treated surfaces with several subtopics such as effects of RF treatments on PET, stabilization of treated PET, study of functional groups created on treated surfaces, effects of the UV radiation on PET, etc.

The third chapter on reinforcement of PET via the addition of carbon-based materials provides details on carbon-based composites, and the authors explain the composites of carbon-based materials with PET carbon-based materials such as carbon nanotubes, carbon fibers, and graphene. This chapter also discusses different topics such as PET-carbon nanotube composites, PET/fiber composites, and PET-graphene composites and their preparation, properties, and applications. The next chapter mainly concentrates on PET-based blends: thermoplastic and thermoset. In this chapter, the authors discuss two main topics, PET-based thermoplastic blends and PET-based thermoset blends. The first topic in this chapter is divided into three subtopics: preparation of PET blends with polyolefins, properties of PET-based thermoplastic blends, and application of PET blends. The second topic is also divided into subtopics: preparation of PET blends with epoxy resin, preparation of PET blends with amide, preparation of PET blends with polycarbodiimides, preparation of PET blends with polyurethane and isocyanate, properties of PET-based thermoset blends, and application of PET-based thermoset blends.

The fifth chapter explains PET-based blends: natural rubber and synthetic rubber. This chapter discusses the preparation of PET-based natural rubber blends, where the authors explain the different preparation methods such as mixing Brabender Plasti-Corder, the two-roll mixing mill, the Haake Rheocord, the twin-screw extruder, and solution casting. The authors also discuss the properties of blends such as the morphology of PET-NR blends, molecular characteristics of PET-NR blends, thermal properties of PET-NR blends, and synthetic rubber-based PET blends, such as PET-SR blends.

In Chapter 6 the author explains different types of characterization methods for analyzing properties of PET-based composites and nanocomposites. Different topics are discussed such as mechanical properties, dynamic mechanical analysis, thermogravimetric analysis, differential scanning calorimetry, scanning electron microscopy, atomic force microscopy, transition



electron microscopy, rheological measurements, X-ray diffraction, and SAXS and WAXS analysis.

The seventh chapter on PET: copolyesters, composites, and renewable alternatives surveys the most relevant aspects related to the preparation and characterization of PET composites and copolyesters, and particularly those incorporating materials/units from renewable origin. Moreover, future developments in renewable PET are foreseen. This chapter begins with a short introduction about the main PET properties and related applications. The next section briefly reviews the main aspects related to preparation, properties, and some applications of PET composites with renewable substrates. Other sections are devoted to synthesis, properties, and potential applications of PET copolyesters incorporating aliphatic- or aromatic renewable-based comonomers. Finally, the current status quo of PET development toward a totally renewable-based material is reviewed.

The eighth chapter, on molecular weight determination of PET, explains different topics such as determination of PET molecular weight, applications of PET, and PET-clay nanocomposites, with many subtopics such as the intrinsic viscosity method, determination of intrinsic viscosity from the melt-flow index, determination of molecular weight by the Mark-Houwink equation, determination of molecular weight by carboxyl and hydroxyl end group assay methods, the mobile phase for the determination of molecular weight of PET by gel permeation chromatography, PET-clay nanocomposites, etc.

Chapter 9 on degradation kinetic parameter determination of blends containing PET and other polymers with nanomaterials discusses thermal characterizations and the parameters of PET-based blends, and thermal degradation of PET when blended with other materials, in order to understand its reaction kinetics and estimate the main kinetic parameters after developing a sound mathematical model that can explain its behavior under heat in inert atmospheres. The authors explain two case studies devoted to this purpose. The first is the study of PET blends with polymethyl methacrylate (PMMA) and the second focuses on polybutylene terephthalate (PBT, another

common polyester) blends with nanoclay and carbon nano fiber. Degradation kinetics were modeled in both cases and the preexponential ( $A_0$ ), activation energy ( $E_a$ ), and reaction order ( $n$ ) were estimated.

The tenth chapter explains the modification of polymer composites by PET waste. In this chapter, the authors explain two main topics, the application of PET waste in construction composites and epoxy mortars modified by PET glycolysate. Many subtopics are discussed related to waste PET modifications such as aggregates and PET waste powder as the aggregate substitute in concrete and mortar, recycled PET fiber reinforcing concrete and mortar, PET waste application in unsaturated polyester resin production, PET waste application for epoxy resin production, uncemented composites prepared with PET waste, the process of obtaining mortar samples, microstructural studies, tensile strength in bending and compressive strength, and water absorption and chemical resistance to selected corrosive media.

Chapter 11 reviews highly functionalized PET for food packaging. In this chapter, the backgrounds of PET-based packaging and its requirements are summarized and discussed in connection with industrial applications of PET. In consequence, two different approaches to improve the mechanical and barrier properties of PET for food packaging were introduced: thin-film coating for effective improvement of barrier properties, and nanofiller blending for the enhancement of the barrier and mechanical properties of PET.

Finally, the editors would like to express their sincere gratitude to all the contributors of this book, who gave excellent support for its successful completion. We are grateful to them for the commitment and sincerity they have shown toward their contributions. Without their enthusiasm and support, this book would not have been possible. We would like to thank all the reviewers who have given their valuable time to make critical comments on each chapter. We also thank the publisher Elsevier for recognizing the demand for such a book, and for realizing the increasing importance of Poly(Ethylene Terephthalate) Based Blends, Composites and Nanocomposites.

**Visakh P.M.**

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# 1 Polyethylene Terephthalate: Blends, Composites, and Nanocomposites – State of Art, New Challenges, and Opportunities

Visakh P.M.

*Department of Ecology and Basic Safety, Tomsk Polytechnic University, Tomsk, Russia*

## OUTLINE

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## 1.1 Modification of Polyethylene Terephthalate

Polymer films need additional surface treatments to modify the surface properties, for better wettability and adhesion activities [1–5]. There are different methods to modify the surface properties of the polymer films such as chemical or plasma treatments, ultraviolet (UV) or laser irradiation.

Polyethylene terephthalate (PET) was selected for study on the basis of the reactivity of its ester group. This polymer was studied in order that good protein adsorption could be achieved onto the polymer surface [6–9] by utilizing the methods discussed hereinafter. PET has excellent mechanical strength, good stability against body fluids, and high radiation resistance for sterilization, but its surface is not favorable for the immobilization

of biomolecules. Plasma modification of PET has been studied by some workers, and changes in the physical behavior and surface morphology have been reported [10–12].

PET has a variable density of zones: a density characteristic of amorphous areas and the crystalline areas. The crystalline region variations in density are attributed to crystal defects caused by the crystallization conditions and the amorphous density variations from conformational restrictions. The orientation of the macromolecules of PET is identified in the literature to be due to *trans* conformer transformation in the *gauche* conformer.

The interfacial tension from the PET surface is reduced just after plasma treatment due to the rapid migration of the polar segments towards the bulk of the polymer. A fraction of the functional groups is transformed into stable structures at the surface



itself, diminishing the surface hydrophilicity. Some authors [13–16] have reported similar observations for the plasma-treated PET films, and have correlated them with the reorganization of the surface, as well as surface contamination during storage.

UV treatment requires a light source that directs UV or visible light onto the formulated product. The substrates absorb the UV energy from the light source, starting a chemical reaction that quickly converts them onto a solid functionalized surface, forming monomers and oligomers. Monomers are low molecular weight materials that can be mono- or multifunctional molecules, depending on the number of reactive groups they possess. Because reactive functional groups of the substrates appear during exposure to UV light, certain new properties are present on the surface of the polymer.

Some authors reported studies on different polymers: polypropylene, polystyrene, polycarbonate, styrene acrylonitrile copolymer, and poly(methyl methacrylate) UV irradiated for various times [17]. The photodegradation related to the extinction coefficient in the UV region generated the accumulated layer of the degraded species. The individual and combined effects of UV light combined with ozone have been studied for many different surfaces, including polypropylene, polyethylene, PET, poly(ether ether ketone), and polystyrene. The surface energy of the polymers increases through the breaking of the polymer chain by insertion of oxygen-containing functional groups due to the ultraviolet treatment. Studies of PET treatment and UV light treatment with excimer UV laser irradiation [18] show a partial surface destruction, caused by thermal effects due to the extremely high pulse-energy density.

Collagen is the foundation of the extracellular matrix in a variety of connective tissues including bone, dentin, cartilage, tendons, dermis, and cornea, and the major structural protein in animals, comprising up to 30% of total protein weight [19,20]. The most attractive feature of plasma and UV processing is that by exerting proper control over the exposure conditions, a tailored surface with desired chemical functionality and morphology may be produced. There are specific biological and chemical criteria that must be taken into consideration when modifying surfaces for biomaterial applications.

In the case of plasma treatment, while the surface roughness is not expected to change with time, the hydrophilicity of plasma-treated PET was found to decrease with time by contact angle measurements.

## 1.2 Reinforcement of Polyethylene Terephthalate via Addition of Carbon-Based Materials

Carbon-based materials including carbon nanotubes (CNTs), carbon fiber, and graphene have extraordinary thermal conductivity and mechanical and electrical properties, thus finding applications as additives to various structural and functional materials. When they are incorporated into a PET polymer matrix, the resulting composites have significantly different electrical, mechanical, and physical–chemical properties than the original.

When CNTs, multiwalled or single walled, are incorporated into a PET polymer matrix, the resulting nanocomposites can have electrical properties that differ from pristine PET [21,22].

PET reinforced by graphene has been prepared by a combination of solution and melt processing and has improved mechanical properties [23]. This reinforcement has been predominantly attributed to the dispersion quality resulting from the solvent exfoliation of both nanotubes and graphene. PET/graphene nanocomposites were prepared by melt compounding and have enhanced the electrical conductivity of PET, resulting in a sharp transition from electrical insulator to semiconductor with a low percolation threshold of 0.47 vol% [24]. PET is beginning to show promise in industrial applications [25–27]. Although promising, the disadvantages, like insufficient mechanical properties and thermal stability and other functional requirements in new fields, have restricted PET's practical application in industry. In this regard, research has been extensively performed to find high performance PET [28–30].

As CNTs have excellent electrical, thermal, and mechanical properties, a number of efforts have been made to incorporate CNTs into PET to develop high performance nanocomposite polymers, in fields ranging from basic science to industrial applications [31]. Thus, CNTs can greatly make up for the disadvantage of PET. PET/CNT composites are prepared by melt compounding metallized polyethylene terephthalate/nanotubes (M-PET/NTs). M-PET was also processed with the same procedure of melt compounding as reference [32].

The PET nanocomposites containing isocyanate groups showed improved mechanical properties, including tensile strength and tensile modulus, compared with those with pristine and acid-treated nanotubes [33]. Various matrix polymers such as polypropylene, polystyrene [34,35], and PET [36]



have been tested and various mechanical properties such as tensile and bending strengths and moduli, yield stress, fracture toughness, fatigue, and friction have been investigated. It has been proved that conductive polymer composites with high electrical conductivity and modified mechanical properties at low CNT loadings can be obtained by preparing *in situ* microfiber-reinforced PET/CNT composites through extrusion and hot stretching.

From the literature the effect of CNTs on the rate of PET crystallization has been investigated through differential scanning calorimetry in transient and isothermal modes, carried out on nanocomposite samples of PET, melted with single walled carbon nanotubes at concentrations of 0–3 wt%.

The various kinds of fillers dispersed in PET can increase the mechanical properties of polymers such as tensile strength, modulus, and fracture toughness. Among the fillers, CNTs have a large aspect ratio [37,38]. By using the properties of CNTs, many excellent properties of composite materials can be produced. For example, the plastics reinforced with CNTs have excellent mechanical properties, good conductivity, corrosion resistance, and can shield radio waves.

Usually, the carbon fibers have been blended into PET matrices using conventional mixing methods, for example a twin-screw extruder [39–41], a high shear mixer [42,43], as well as a two-roll mill [44]. G. Morales et al. [45] prepared CNF/PET composites by compounding methods included ball milling, high shear mixing in the melt, as well as extrusion using a twin-screw extruder. G. Morales et al. [46] studied PET/short carbon fiber composites by melt extrusion processing. Carbon fiber-reinforced polybutylene terephthalate (PBT) composites have shown superiority due to their outstanding mechanical properties as well as their light-weight characteristics [47].

J. Martinsson et al. [48] studied the recycled carbon fiber-reinforced PBT. The mechanical properties, heat distortion temperature, and thermal stability of PBT could be significantly improved by incorporating this surface-treated carbon fiber. Carbon-reinforced PET materials have extensive application in the area of health monitoring for the employment of neural networks [49].

PET fibers are most extensively used in textiles and can be produced with Young's modulus, strength, and tensile toughness up to  $\sim 10$  GPa,  $\sim 1$  GPa, and  $200 \text{ MJ/m}^3$ , respectively [50]. However, one merit of PET fibers is that they can be melt-spun, cheaply and in large quantities [51].

### 1.3 Polyethylene Terephthalate-Based Blends: Thermoplastic and Thermoset

PET blends can be typically prepared by five techniques: graft copolymerization, melt solution, latex blending, partial block, and synthesis of interpenetrating networks. Melt blending is a simple mechanical process of creating a homogeneous mixture of two or more polymers. The major advantage of melt blending is the absence of any solvents that might be required in other methods of polymer blending [52].

PET possesses hydroxyl and carboxyl functional groups at chain ends; *in situ* or reactive compatibilization is an effective approach for developing engineering thermoplastic blends from these materials. Sometimes, a reactive coupler, such as epoxide moiety, maleic anhydride, glycidyl methacrylate, etc., is used to compatibilize thermoplastic PET blends. The combination of PET with polyolefins represents yet another important group of PET blends. The use of recycled scrap from PET and polyolefins for ecological reasons, especially from soft drinks bottles, etc., is the main reason for developing blends of PET with polyolefins. High-density polyethylene (HDPE) and PET contain a major portion of postconsumer waste and are recycled to reduce waste, especially from packaging. Blending of these polymers is an alternative method to reduce waste. However, HDPE and PET are immiscible [53]. Through a proper compatibilization strategy, the blends can combine the stiffness (dimensional stability) of PET with the good impact strength of HDPE.

Akkapeddi and Van Buskirk [54] studied the compatibilization of postconsumer PET/HDPE blends. The melt blends were prepared in a single-screw extruder and a corotating twin-screw extruder. Iniguez et al. [55] studied the morphological stability of postconsumer PET/HDPE blends at different compositions (10–90% by volume of PET in HDPE) with and without a compatibilizer. Kim et al. [56] studied the compatibilization of PET/HDPE blends. High-density polyethylene grafted with the blocked isocyanate group was used as a reactive compatibilizer for an immiscible PET/HDPE blend.

Murff et al. [57] prepared a melt blend of polycarbonate and PET by continuous extrusion and injection molded it into bars to study their thermal and mechanical behavior. Huang [58] studied and discussed the mechanism, morphology, and mechanical properties of PET/PA-6 (polyamide-6) blends with low molecular weight bisphenol-A epoxy resin

(E-44) as a reactive compatibilizer. Imashiro et al. [59] have described adding a carbodiimide compound to recycled PET such that the intrinsic viscosity and strength of the polyester resin during processing are retained.

## 1.4 Polyethylene Terephthalate-Based Blends: Natural Rubber and Synthetic Rubber

PET is a very important engineering thermoplastic polyester because of its excellent chemical resistance, good mechanical and thermal properties, as well as its excellent optical and barrier properties, which make PET an ideal candidate for use as beverage bottle applications.

The effect of compatibilization between rubber and a PET matrix has been observed to play an important role in the resulting blend's behavior [60–62]. Rubber modification gives an effective method for enhancing the impact behavior of notch-sensitive PET [63,64]. The main role of the dispersed rubber particles is to induce a global deformation mechanism, rather than a localized type.

Based on theories of rubber toughening [65], blend morphologies and characteristics, such as average rubber particle size and concentration of the dispersed phase, will have distinct influences on the final mechanical properties. The PET/NR (natural rubber) blends are normally prepared in the laboratory via mixing in a Banbury mixer or Brabender Plasti-Corder attached to a mixer or a twin-screw compounder. The dried PET is first melted in the mixer and then masticated NR is added [66]. Additives, such as compatibilizers or stabilizers are added before the addition of the NR [67].

An unstable morphology and poor interfacial adhesion will result in a blend with poor mechanical properties. To viably develop a PET/NR blend with a desired fine phase morphology, the use of a reactive compatibilization strategy plays an important role, when two polymers are immiscible. Blends of PET and NR were prepared by Phinyocheep et al. [68] in different ratios by the twin-screw extruder technique. PET is dried in an air oven at 120°C for 10 h in order to avoid excessive moisture-induced degradation reactions, before processing in a corotating twin-screw extruder. The notch sensitivity of PET becomes quite apparent from the very low notched Izod impact strength (6.0 J/m) that was obtained by passing the PET in the twin-screw extruder before injection molding into test specimens.

PET/NR blends possess excellent properties, such as reduced permanent set, improved mechanical properties, greater resistance to attack by fluids, improved high temperature utility, etc. [69], and therefore provide very useful and attractive applications in different fields, for example automotive parts, building materials and construction equipment, wire and cable insulation, etc. [70]. PET/NR blends are generally used for making automobile parts where operations such as abrasion, flexing, and tear are prominent factors leading to the fracture of the products [71].

PET is an engineering plastic and is widely used as an engineering thermoplastic often in packaging, electronics, and other applications [72]. PET online viscosity presents a substantial decrease, due to thermomechanical degradation at the processing conditions [73]. It is important to note that the viscosity variation with shear rate, in the physical blends, is such that the viscosity curves lie above the PET curve. The rubber particles infuse an increasing resistance to flow, as observed in polymer-filler systems [74].

Lashgari et al. [75] reported that PET/ABS (poly(acrylonitrile-co-butadiene-co-styrene)) blends with more ABS content have higher impact resistance, thus attesting to the good impact property of ABS. On the other hand, the impact strength of the blends increases with MAH content, a finding that suggests that using grafted ABS, instead of neat ABS, enhances the impact strength through the compatibilizing process, because of the bond formation between functional groups of PET and ABS-g-MAH.

## 1.5 Characterization of Polyethylene Terephthalate-Based Composites and Nanocomposites

PET is a plastic resin and is the most common type of polyester used commercially. It is also one of the most recycled plastics in the market. Microstructure and mechanical properties of PET can be significantly controlled by tailoring crystallization rate and degree of crystallinity with use of additives [76–79]. The role that nanoparticles play in the crystallization behavior of PET nanocomposites is widely reported in the literature [80,81]. Ou et al. [82,83] in their report have suggested that half-life of crystallization can be lowered on clay intercalation in PET.

Investigations by Barber et al. [84] have shown that the incorporation of organically modified montmorillonite (MMT) clays, such as Cloisite® 30A, via solution blending can significantly increase the crystallization temperature while lowering the crystallization half-time.