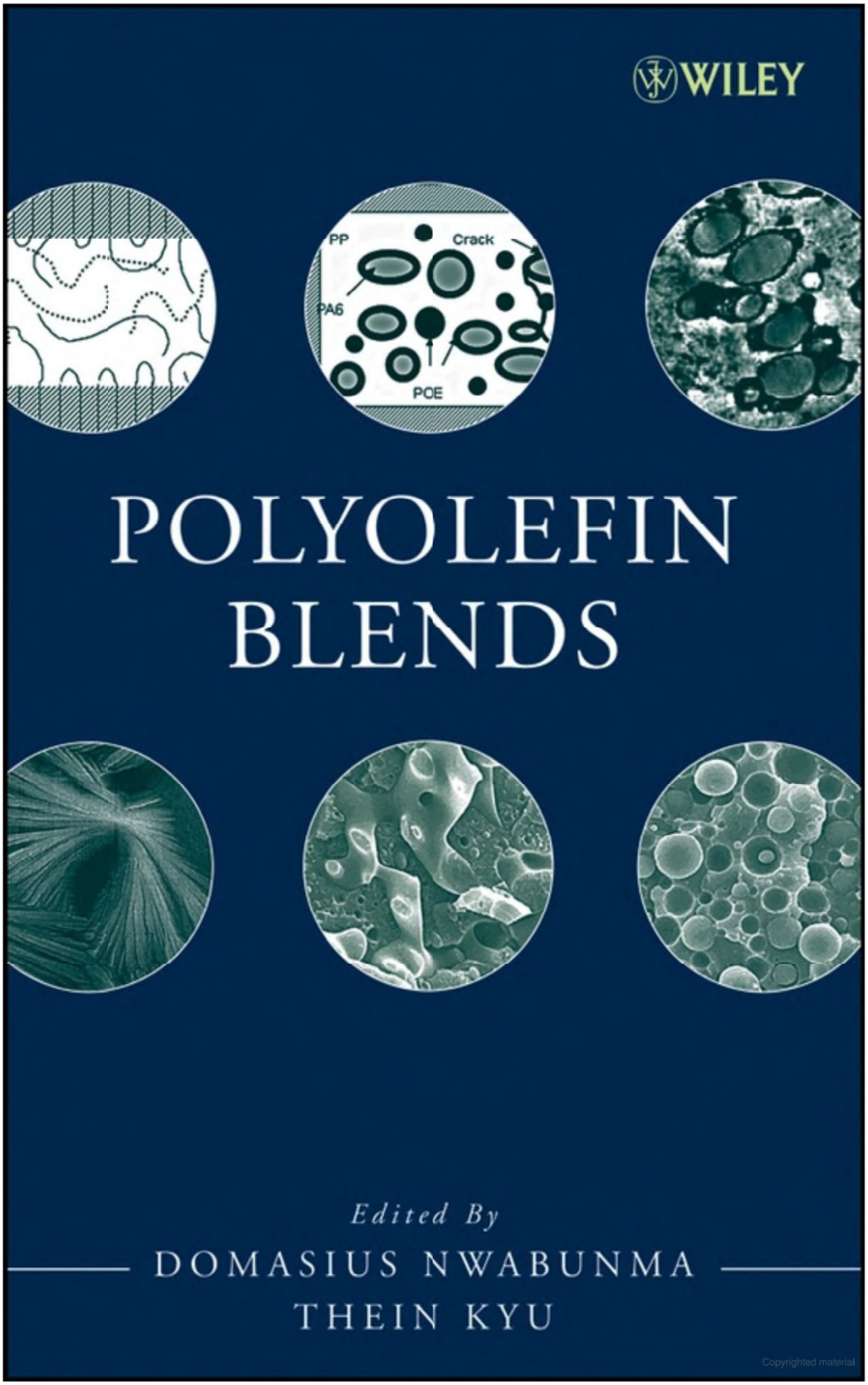
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Chapter 1

Overview of Polyolefin Blends

Domasius Nwabunma[1]

1.1 INTRODUCTION

Polyolefins are synthetic polymers of olefinic monomers. They are the largest polymer family by volume of production and consumption. Several million metric tons of polyolefins are produced and consumed worldwide each year, and as such they are regarded as commodity polymers. Polyolefins have enjoyed great success due to many application opportunities, relatively low cost, and wide range of properties. Polyolefins are recyclable and significant improvement in properties is available via blending and composite technologies.

Polyolefins may be classified based on their monomeric unit and chain structures as ethylene-based polyolefins (contain mostly ethylene units), propylene-based polyolefins (contain mostly propylene units), higher polyolefins (contain mostly higher olefin units), and polyolefin elastomers (1). Ethylene-based polyolefins are normally produced either under low pressure conditions using transition metal catalysts resulting in predominantly linear chain structure or under high pressure conditions using oxygen or peroxide initiators resulting in predominantly branched chain structures of various densities and crystallinity levels.

Propylene-based polyolefins are normally produced with transition metal catalysts resulting in linear chain structures with stereospecific arrangement of the propylene units or special stereoblock structures from a single-site catalyst. Higher polyolefins are normally produced using transition metal catalysts resulting in linear and stereospecific chain structures. Polyolefin elastomers based mainly on a combination of ethylene and propylene may be produced using metal or single-site catalysts with or without the inclusion of dienes (for cross-linking) and are mostly amorphous with high molecular weights and heterogeneous in phase structures. One

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may conclude that a given polyolefin may be a homopolymer, copolymer, or terpolymer depending on the number of monomers used in making the polyolefin, crystalline or amorphous depending on their chain conformation, configuration, and processing conditions.

Today, polyolefins and polyolefin-based materials are used in many applications. These applications include transportation (automotive, aerospace), packaging, medical, consumer products (toys, appliances, etc.), electronics, cable and wire coating, thermal and acoustic insulation, and building and construction. Polyolefins can be extruded as filaments (fibers), films (cast and blown), and pipes/profiles. They can be molded into parts of various shapes. They can be foamed with physical and chemical foaming/blowing or/and can be coated onto other materials.

1.2 OLEFINIC MONOMERS

The alkenes having one or more unsaturated double bonds in their structures are the monomers used to synthesize polyolefins. They have the general formula C_nH_{2n}, $n \geq 2$. Table 1.1 shows the first 10 members of the olefinic monomers with one double bond, which are often called α-olefins.

The monomers in Table 1.1 form a homologous series of hydrocarbon compounds. Thus, apart from having the same general formula, all compounds in the series have the same functional groups. Each member of the group differs from the next in the series by the CH_2 group equivalent to 14 relative molecular mass units.

All members of the series have similar chemical properties. The physical properties of the compounds in the series show a progressive change with increasing relative molecular mass. The first three members of the alkenes homologous series are gases at room temperature. Those containing between 5 and 15 carbon atoms are colorless liquids and the higher compounds are waxy solids at room temperature. These α-olefinic monomers may be obtained as products of the cracking of the gas–oil and naphtha fractions of petroleum distillations. They can also be obtained from synthetic organic chemistry methods.

Table 1.1 Alkene Monomers with One Double Used in the Synthesis of Polyolefins.

No. of carbon atoms (n)	Formula (C_nH_{2n}, $n \geq 2$)	Name (other name)
2	C_2H_4	Ethene (ethylene)
3	C_3H_6	Propene (propylene)
4	C_4H_8	Butene-1 (butylene)
5	C_5H_{10}	Pentene-1
6	C_6H_{12}	Hexene-1
7	C_7H_{14}	Heptene-1
8	C_8H_{16}	Octene-1
9	C_9H_{18}	Nonene-1
10	$C_{10}H_{20}$	Decene-1

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1.3 POLYOLEFIN HOMOPOLYMERS, COPOLYMERS, AND TERPOLYMERS

Polyolefin homopolymers, copolymers, and terpolymers are foundation materials for polyolefin blends. They may be obtained via radical or ionic chain growth polymerization of alkenes using conventional free radicals (e.g., from peroxides) and organometallic complexing (Ziegler–Natta and metallocenes) catalyst systems. Polyolefin polymerization technologies and novel catalyst systems have enabled the rapid development of polyolefins with a wide range of molecular chain structures, morphologies, properties, and particle size and shape.

Polyolefin homopolymers include polyethylene (PE), polypropylene (PP), polybutene-1 (PB), polymethylpentene-1 (PMP), and higher polyolefins. Table 1.2 shows the structures of commercial polyolefin homopolymers.

Of these, PE and PP are the largest by amount produced yearly by the global polyolefin companies (1). PE comes in various forms differing in chain structures, crystallinity, and density levels. These are high density polyethylene (HDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), ultralow density polyethylene (ULDPE), and ultrahigh molecular weight polyethylene (UHMWPE). PP and higher polyolefins come in three stereospecific forms of varying densities: isotactic, syndiotactic, and atactic forms.

Polyolefin copolymers involve two olefinic monomers. The process of copolymerization is normally used to control the properties of the polyolefins. Some of the consequences of copolymerization are reduced crystallinity, melting point, modulus, strength, hardness, and low temperature impact. Polyolefin copolymers are either random or block copolymers of same or different monomers and may be a single phase or heterophasic depending on the amount of comonomer, the polymerization catalyst, and the process. For polyolefin copolymer of same monomers, this can be achieved by having different segments of the copolymer with different tacticities. One can have polyolefin block copolymers of same block or of varying block lengths. One can also have polyolefin copolymers consisting of both block and random segments together in the same macromolecule. Polyolefin copolymers are usually not homogeneous in composition but are actually mixtures of copolymers of varying compositions. It is also possible with polyolefins to have block copolymers with only one monomer. These are called stereoblock copolymers and can be achieved by having sections of the polyolefin copolymer possess different tacticities.

Polyolefin copolymers started with LLDPE and ethylene–propylene rubber (EPR). Today, there are polyolefin copolymers of ethylene with butene-1, hexene-1, octene, cyclopentene, and norbornene and copolymers of propylene with butene-1, pentene-1, and octene-1 in addition to ethylene. There are copolymers of butene-1 with pentene-1, 3-methylbutene-1, 4-methylpentene-1, and octene in addition to its copolymers with ethylene and propylene. There are copolymers of 4-methylpentene-1 with pentene-1 and hexene-1 in addition to its copolymers with butene-1 and propylene. The function of the comonomers is to reduce crystallinity, as compared to the homopolymers, resulting in copolymers that are highly elastomeric with very low

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Table 1.2 Structures of Commercial Polyolefin Homopolymers.

Name (other name)	Chemical structure (repeat unit)
Polyethylene (polyethene, polymethylene)	$-\!\!\left(CH_2-CH_2\right)_n\!\!-$
Polypropylene (polypropene)	$-\!\!\left(CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}\right)_n\!\!-$
Polybutylene (polybutene-1)	$-\!\!\left(CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{\underset{\displaystyle CH_2}{\underset{\vert}{CH}}}}\right)_n\!\!-$
Polyisobutylene (polyisobutene-1)	$-\!\!\left(CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{\overset{\displaystyle CH_3}{\overset{\vert}{C}}}}\right)_n\!\!-$
Polybutadiene	$-\!\!\left(CH-CH=CH_2-CH_2\right)_n\!\!-$
Poly-4-methylpentene-1	$-\!\!\left(CH_2-\underset{\displaystyle CH_3\ \ CH_3}{\underset{\vert}{\underset{\displaystyle CH_2}{\underset{\vert}{\underset{\displaystyle CH_3}{\underset{\vert}{CH}}}}}}\right)_n\!\!-$
Polyisoprene	$-\!\!\left(CH_2-\overset{\displaystyle CH_3}{\overset{\vert}{C}}=CH-CH_2\right)_n\!\!-$

glass transition temperatures, high impact strength, low modulus, low density, and are often optically transparent. The most widely used multiphase polyolefin copolymer is polypropylene impact copolymer. These copolymers are typically composed of isotactic polypropylene (iPP) and EPR. Impact polypropylene copolymers are produced by various processes, but are generally characterized by the synthesis of iPP in the first reactor and EPR in the second reactor. Therefore, these systems are typically reactor blends. Postreactor blending can be done, but the starting material is most often the reactor blend polypropylene copolymer. Polyolefin copolymers are often used for film applications or as impact modifiers.

Polyolefin terpolymers contain three olefinic monomers. A well-known example is ethylene propylene diene monomer (EPDM). The diene (double bond) monomer is

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usually ethylidene norbornene or 1,4-hexadiene. EPDM was introduced because of the difficulty in cross-linking saturated polyolefin homopolymers and copolymers.

There are also functionalized polyolefins. These are usually copolymer or terpolymer containing functional groups like epoxide, anhydride, hydroxyl, acrylate, and carboxylic acid. These functional groups are either grafted onto the polyolefin after polymerization or added directly *in situ* during polymerization reactions involving olefins and functional groups bearing polar monomers such as vinyl acetate, methyl acrylate, butyl acrylate, glycidyl methacrylate, and acrylic acid. Functionalized polyolefins are useful compatibilizers and impact modifiers in blends and composites containing polyolefins and nonpolyolefins. In this sense, functionalized polyolefins may be considered as additives rather than matrix materials in formulation of polyolefin blends.

Commercial polyolefins often contain additives such as colorants, flame retardants, antioxidants, light stabilizers, nucleating agents, antistatic agents, lubricants (microcrystalline waxes, hydrocarbon waxes, stearic acid, and metal stearates), and so on. These additives aid the processing and fabrication of products from polyolefins. Detailed treatments about specific polyolefins, polymerization systems/mechanism/processes, structures, properties, processing, and applications may be found in References 2–9.

1.4 POLYOLEFIN BLENDS

Polymer blends (mixtures of structurally different polymers (10–19)) are of interest because synthesized polymers have not satisfied increasing application demands. Polyolefin blends are a subset of polymer blends and may be classified into two groups. The first group contains polyolefins only, which are formulated to broaden the range of structures, properties, and applications offered by polyolefins. The second group contains polyolefins and nonpolyolefins, which are formulated to mitigate some of the property drawbacks of the polyolefin or the nonpolyolefin. For a blend to be classified as a polyolefin blend, it is presumed that the polyolefin component is of significant composition in the blend.

In terms of miscibility, polyolefin blends may also be classified as miscible and immiscible blends (10, 11). Polyolefin blending requires knowledge of the miscibility and crystallinity of the blend, in addition to the contributions of the components of the blend. Miscibility depends on molecular structure, blend composition, and mixing temperature. To characterize miscibility, a phase diagram is needed.

Nonolefinic thermoplastic polymers that in principle may be blended with polyolefins include polyamides (nylons) such as polyamide 6, polyamide 66, polyphenylene sulfide (PPS), polyphenylene ether (PPE), and polyphenylene oxide (PPO); polyesters such as polyethylene terephthalate (PET), polybutylene terephthalate (PBT), polyethylene naphthalate (PEN), polytrimethylene terephthalate (PTT), polycarbonates, polyethers, and polyurethanes; vinyl polymers such as polystyrene (PS), polyvinyl chloride (PVC), polymethylmethacrylate (PMMA), and ethylene

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vinyl acetate copolymer (EVA); block and graft copolymers (styrene–acrylonitrile copolymer, styrene–butadiene copolymer, styrene–ethylene–butadiene–styrene terpolymer, etc.); and liquid crystalline polymers (LCPs). Thermosetting resins that may be blended with polyolefins include, but are not limited to, the following: epoxies, unsaturated polyesters, phenol formaldehyde, melamine formaldehyde, urea formaldehyde, silicones, and so on.

The properties that polyolefins normally contribute in blends with other polymers include high melt strength and elasticity, toughness, low viscosity for processability, low polarity, dielectric constant, and loss, and chemical resistance and moisture absorption resistance. Nonpolyolefins contribute to high modulus, heat resistance, and oxygen or solvent barrier properties. For example, barrier properties of polyolefins can be improved by blending with polymers such as ethylene vinyl alcohol and polyvinylidene chloride. Blends of polyolefins with nylons and polycarbonate (PC) allow balanced control of permeability and water retention. Polystyrene (PS) is an interesting candidate for blending with polyolefins for mechanical reasons as well as for paintability and printability.

There are two classes of polyolefin blends: elastomeric polyolefin blends also called polyolefin elastomers (POE) and nonelastomeric polyolefin blends. Elastomeric polyolefin blends are a subclass of thermoplastic elastomers (TPEs). In general, TPEs are rubbery materials that are processable as thermoplastics but exhibit properties similar to those of vulcanized rubbers at usage temperatures (19). In TPEs, the rubbery components may constitute the major phase. However, TPEs include many other base resins, which are not polyolefins, such as polyurethanes, copolyamides, copolyesters, styrenics, and so on. TPEs are now the third largest synthetic elastomer in total volume produced worldwide after styrene–butadiene rubber (SBR) and butadiene rubber (BR).

Two important types of elastomeric polyolefin blends are reactor-made iPP/EPR blends and postreactor blend iPP/EPDM. The latter is called thermoplastic vulcanizates (TPVs), produced by dynamic vulcanization of blends containing a thermoplastic and an elastomer. To make iPP/EPDM TPV, the two polymers PP and EPDM are mixed with curatives, such as peroxides, phenolic resins, or sulfur with accelerators, and dynamically cured in an extruder resulting in a blend consisting of micrometer-sized elastomer particles dispersed in the PP matrix (20–24). Paraffinic oils are added in the melt mixing process for viscosity control and cost. In iPP/EPDM TPV, the crystalline iPP resin is normally the minor phase. Recently, polyolefin plastomers have been added to the class of elastomeric polyolefin blends. Polyolefin plastomers are ultralow molecular weight linear low density polyethylenes (ULMW-LLDPE). Nonelastomeric polyolefin blends are blends of polyolefins with mostly nonpolyolefin (other thermoplastic) matrices as mentioned earlier.

Polyolefin blends of commercial importance are normally made via two methods: blending in the melt either during polymerization or mechanically after the polymerization process. The first method, called in-reactor blending, involves the blending of different polyolefins (homopolymers, random, and block copolymers) in a polymerization reactor. This is enabled by the presence of multiple catalyst species

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in the polymerization recipe. A good example is in-reactor-made EPR/iPP blend, which is normally prepared by adding ethylene monomer to propylene monomer toward the end of propylene polymerization process. The function of EPR is to improve iPP flexibility; hence, EPR/iPP blend is often called toughened or impact PP and finds wide applications in the consumer industry. Another good example of in-reactor-made polyolefin blend is linear low density polyethylene (LLDPE), which often contains several ethylene/α-olefin copolymers that differ in ethylene contents. LLDPE and reactor-made EPR/iPP are often called thermoplastic olefins (TPOs).

The second method, called postreactor blending, involves mechanical blending of a premade polyolefin with other polyolefins or nonpolyolefins in compounding extruders. A practical example of polyolefin blend made using this method is a blend of isotactic PP with cured EPDM, as described earlier. Other examples of polyolefin blends made by postreactor mechanical blending include polyolefin/polyamides (nylons), polyolefin/polyesters, polyolefin/polystyrene (PS), polyolefin/polyvinyl chloride (PVC) blends, and so on. EPR/iPP blend can also be made by postreactor mechanical blending as well as by in-reactor blending. Postreactor blending via single and twin screw compounding is still the preferred method of polyolefin blending because it is quick, easy, economical, and efficient.

Table 1.3 shows a summary of specific polyolefin blends that have been studied in the literature extracted from references (25–310). These blends involve the following polyolefins: PP, PE (LLDPE, LDPE, HDPE, and UHMWPE), EPR, EPDM, and PB. Some of the blends listed in Table 1.3 are of commercial importance (6).

There are many publications (journal articles and patents) on polyolefin blends in the literature. Tables 1.4 contains a summary of the journal articles (25–310) and patents published each year during the 6-year period 2000–2005.

The choice of date range is arbitrary. The number of journal articles for each year was obtained from a search of electronic version of English-based polymer and polymer-related journals using the keywords polyolefin and blends. Within polyolefin keyword, the subkeywords used in the search were polyethylene (PE, LLDPE, LDPE, HDPE, UHMWPE, PE, etc.), polypropylene (PP, iPP, sPP, aPP, etc.), polybutene-1, poly-4-methylpentene-1, ethylene–diene monomer, ethylene–propylene–diene terpolymer, ethylene propylene rubber, thermoplastic olefins, natural rubber (NR), polybutadiene, polyisobutylene (PIB), polyisoprene, and polyolefin elastomer. For the polyolefin blends patent search, polymer indexing codes and manual codes were used to search for the patents in Derwent World Patent Index based on the above keywords listed in the search strategy.

Table 1.4 shows an increasing trend in the number of publications. It should be noted that while generating Table 1.4, some publications may have been missed in the reference search period (2000–2005).

There are several issues of interest in polyolefin blends research. They may be categorized into formulation design and processing; miscibility, structural, molecular, and property characterization; end-use properties and performance; and

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Table 1.3 Polyolefin Blends Studied in the Literature.

Polyolefin blends		
HDPE/UHMWPE (81)	PE/PP/EPR (35, 114)	PP/PET (137)
LDPE/HDPE (84, 153, 160, 221, 259, 284)	PE/PC (29, 173, 213)	PP/PE/EPDM (49)
LLDPE/HDPE (285)	PE/poly(silsesquioxanes) (156)	PP/EVOH (135, 298)
LLDPE/LDPE (72, 104, 108, 119, 128, 129, 181, 211, 214, 221, 242, 258, 261, 292, 309)	PE/ethylene acrylic elastomer (281)	PP/PA66 (28)
LLDPE/LDPE/wax (80)	PE/PP/PA6 (71)	PP/PA6 (28, 54, 58, 71, 111, 170, 178, 262, 283, 286, 288, 305)
PE/PA6 (25, 27, 71, 88, 92, 96, 130, 140, 144, 149, 168, 204, 215, 224, 226, 272, 273)	PE/PS (47–48, 67, 79, 123, 145, 198, 219, 223)	PP/PA6/ethylene-co-octene (28, 31, 43, 46)
PE/PP (33, 34, 36, 47, 62, 69, 83, 93, 107, 116, 182, 196, 200, 203, 236, 237, 239, 243, 248, 255, 263, 297)	PE/PP/PA66 (71)	PP/PB (26, 109)
PE/PP/cycloolefin copolymers (307)	PP/PPE (216, 217)	PP/PC (25)
PE/ethylene-co-propylene-co-butene-1 (99)	PP/EPDM (50, 66, 113, 121, 136, 199, 202, 207, 224, 267)	iPP/sPP (40); iPP/aPP (103)
PE/polydianilinephosphazene (91)	PP/EPR (35, 63, 77, 118, 124, 152, 163, 195, 231, 233, 271)	PP/EPDM/natural rubber (244–246)
PE/silicon rubber (76)	PP/epoxy (62, 120)	PP/EPDM/epoxidized natural rubber (246)
PE/starch (85, 277, 289, 295)	PP/PA6/PS (205)	PP/epoxidized natural rubber (301)
PE/hydrolyzed collagen (98)	PP/cyclopolyolefin (162)	Butadiene/styrene–butadiene rubber (293)
PE/natural rubber/PP (238, 254, 302)	PP/natural rubber (64, 241, 247, 287)	EPDM/PA66
PE/poly(3-hydroxybutyrate) (251)	PP/recycle rubber(241, 247)	EPDM/SBR (68)
PE/nitrile rubber (100, 183)	PP/natural rubber/recycle rubber powder (249)	EPDM/NBR (234)

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PE/PA12 (142)
PE/PTT (37)
PE/PVC (52, 201)
PE/starch/PCL (90)
PE/ethylene-co-octene (46, 278)
PE/ethylene-co-butene-1 (89, 171)
PE/PA6,6 (127, 169, 273)
PE/perfluoropolyether (126)
PE/EVA (45, 51, 56, 78, 97, 161, 270)
PE/PET (166, 167, 208, 213, 220, 274)

PE/PBT (82, 300)
PE/PS/PMMA (209)
PE/wax (256)

PP/ethylene-co-methyl acrylate (164)
PP/P12 (304)
PP/TPU (228)
PP/SBS (74)
PP/SAN (184)
PP/EVA (177, 189, 191, 193, 294)
PP/SEBS (74, 112, 218)
PP/SEP (105, 218)
PP/SEPS (105, 218)
PP/PS (38, 39, 117, 155, 159, 227, 212, 229, 299, 310)
PP/ethylene-co-octene (59, 87)
PP/ethylene-co-butene-1 (59)
PP/LCP (225, 232)

EPDM/SAN (53, 308)
EPDM/PA6 (101, 279)
EPDM/polyaniline (122)
EPDM/TPU (95)
EPDM/PP/PA6 (262)
EPDM/PA12,10 (262)
EPDM/PP6,10 (266)
EPDM/natural rubber (44, 65, 240, 250, 269)
EPR/polydimethylsiloxane (70)
EPR/PA6 (57, 60)

Natural rubber/polystyrene (290)
Natural rubber/reclaimed rubber (252)
Epoxidized natural rubber/natural rubber (253)

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Table 1.4 Summary of Number of Electronic articles on Polyolefin Blends Published Between 2000 and 2005 in English Language-based Polymer and Polymer-related Journals in Comparison to the Number of Patents.

	Journal articles (25–310)						
Year	2000	2001	2002	2003	2004	2005	Total
Number of Articles	36	31	42	42	68	66	285
	Patents						
Year	2000	2001	2002	2003	2004	2005	Total
Number of Patents	517	444	406	295	322	365	2349

modeling and simulation. Regarding formulation design and processing, some of the issues of interest include

i. Use of block, random, and graft copolymers in compatibilization.

ii. Effects of molecular structure, weight, and additives.

iii. Phase behavior, miscibility, and compatibility issues.

iv. Batch and continuous mixing/compounding, extrusion, and molding into films, fibers, and other articles.

v. Physical blending versus reactive blending.

Regarding miscibility, structural, molecular, and property characterization, some of the issues of interest include

i. Morphological characterization using techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), and polarized light microscopy (PLM).

ii. Structural characterization using radiation scattering and diffraction techniques such as X-ray scattering (XRS), X-ray diffraction (XRD), and electron diffraction (ED).

iii. Structural characterization using spectroscopic techniques such as nuclear magnetic resonance (NMR), Fourier transform infrared (FTIR), and temperature rising elution fractionation (TREF).

iv. Melt rheology.

v. Phase separation dynamics.

vi. Thermal transitions and thermal stability.

vii. Isothermal and nonisothermal crystallization behavior under quiescent and nonquiescent conditions.

viii. Crystallinity and crystal structure determination by various methods such as density, differential scanning calorimetry (DSC), XRD, and ED.

ix. Tacticity, copolymer sequence distribution, and comonomer composition.

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Regarding end-use properties and performance, some of the issues of interest include

- **i.** Mechanical (static and dynamic) behavior under tensile, shear, or compressive, and impact mode.
- **ii.** Plastic deformation.
- **iii.** Thermomechanical and thermal stability behavior.
- **iv.** Adhesion, interfacial, and interphase behavior.
- **v.** Fire resistance/flammability behavior.
- **vi.** Barrier and transport properties.
- **vii.** Optical properties (gloss, haze, and transparency).
- **viii.** Surface/tribological properties.
- **ix.** Electrical/dielectric properties.
- **x.** Aging effects (time–temperature-dependent behavior).

Modeling and simulation involves theoretical analysis of processing, characterization, and performance behavior using phenomenological, atomistic, molecular dynamics, and Monte Carlo methods, among others, and comparisons with experimental results.

Polyolefin blends are generally immiscible due to hydrophobic or nonpolar nature of polyolefins. The immiscibility leads to phase separation, which is responsible for the poor mechanical properties of these blends. Immiscibility of polyolefin/nonpolyolefin blends can be mitigated by adding a proper compatibilizer. The function of a compatibilizer is to reduce interface tension (strengthen the interface between the phases) and thus improve mechanical properties of the stabilized blend (reduce the size and morphology of the phase-separated phases). The compatibilizer strengthens the interface by broadening it from a sharp change in composition and properties to a broader gradual transition interface. Thus, the chief concern in compatibilization of polyolefin/nonpolyolefin blends is phase morphology.

One way to achieve compatibilization involves physical processes such as shear mixing and thermal history, which modify domain size and shape. The second way is the use of physical additives to increase attraction between molecules and phases. The third method is reactive processing, which is used to change the chemical structure of one or more of the components in the blend and thus increase their attraction to each other. Table 1.5 contains a list of compatibilizers used in the formulation of polyolefin blends. As can be seen from Table 1.5, most of the compatibilizers used in the formulation of polyolefin blends contain compounds such as maleic anhydride, acrylic and methacrylic acid, glycidyl methacrylate, and diblock and triblock copolymers involving styrene, ethylene, and butadiene.

1.5 TRENDS IN POLYOLEFIN BLENDS

The first trend is the growing use of in-reactor blending technique to produce new elastomeric or toughened polyolefins for demanding applications traditionally reserved

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Table 1.5 Compatibilizers Used in the Formulation of Polyolefin Blends.

Compatibilizer	Polyolefin blend
PP-g-maleic anhydride	PE/PA6 (27, 88)
Ethylene-co-acrylic acid	PE/PA6 (27, 92, 140, 204, 215, 224)
Ethylene-co-glycidyl methacrylate	PE/PA6 (27, 144)
Styrene-b-ethylene-co-propylene-g-maleic anhydride	PE/PA6 (130)
PE-g-maleic anhydride	PE/PA6 (130)
Styrene-co-ethylene-co-butadiene-co-styrene-g-maleic anhydride	PE/PA6 (130, 168)
Sodium-neutralized ethylene-co-methacrylic acid	PE/PA6 (92)
PE-g-glycidyl methacrylate	PE/PA6 (144)
Styrene-co-ethylene-co-butadiene-co-styrene-g-glycidyl methacrylate	PE/PA6 (168)
Styrene-co-ethylene-co-butadiene-co-styrene	PE/PP/PA6,6 (71)
Styrene-co-ethylene-co-butadiene-co-styrene-g-maleic anhydride	PE/PP/PA6,6 (71)
PE-g-maleic anhydride	PE/PA12 (142)
EPR-g-maleic anhydride	PE/PP (47)
PE-g-maleic anhydride	PE/PP (71, 239)
PP-g-maleic anhydride	PE/PP (71, 239)
Styrene-co-ethylene-co-butadiene-co-styrene	PE/PS (47)
Styrene-co-butadiene	PE/PS (48, 115)
Styrene-co-ethylene-co-butadiene-co-styrene	PE/PS (79)
Styrene-co-butadiene-co-styrene	PE/PS (145)
Liquid polybutadiene + diakyl peroxides	PE/PS (223)
Chlorinated PE	PE/PVC (52)
Ethylene-co-acrylic acid	PE/hydrolyzed collagen (98)
Bismaleimide-g-PE	PE/hydrolyzed collagen (98)
PE-g-maleic anhydride	PE/acrylonitrile-co-butadiene (100)
PE-g-epoxidized natural rubber	PE/scrap rubber powder (165)
PE-g-diethyl maleate	PE/PET (166)
Sodium neutralized ethylene-co-acrylic acid	PE/LCP (188)
PE-g-glycidyl methacrylate	PE/PET (220)
PE-g-maleic anhydride	PE/ethylene-co-acrylic acid (281)
Ethylene-co-glycidyl methacrylate	PE/plasticized tapioca starch (289)
Styrene-co-ethylene-co-butadiene-co-styrene	PP/PA6,6 (28)
Styrene-co-ethylene-co-butadiene-co-styrene	PP/PA6 (28)
PP-g-3-isopropenyl-α,α-dimethylbenzene isocyanate	PP/PA6 (54)
PP-g-succinic anhydride and PP-g-fluorescein	PP/PA6 (111)
PP-g-maleic anhydride	PP/PA6 (58, 170, 178, 262, 283, 286, 289)
Ethylene-co-butyl acrylate-g-maleic anhydride	PP/PA6 (170)
Styrene-co-ethylene-co-butadiene-co-styrene-g-glycidyl methacrylate	PP/PA6 (178)

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Table 1.5 (*Continued*)

Compatibilizer	Polyolefin blend
PP-g-bismaleimide	PP/PA6 (262)
PP-g-acrylic acid	PP/PA6 (262)
EPDM-g-maleic anhydride	PP/PA6 (279)
Ethylene-co-octene-g-maleic anhydride	PP/PA6 (286)
PP-g-maleic anhydride	PP/epoxy (62, 120)
Styrene/$AlCl_3$-catalyzed friedel–crafts alkylation	PP/PS (21, 117)
PP-g-PS	PP/PS (155, 299)
Styrene-co-ethylene-co-butadiene-co-styrene	PP/PS (299)
Styrene-co-ethylene-co-butadiene-co-styrene + ionomer resin	PP/PS/PA6 (205)
Ionomer Zn^{2+}	PP/EVOH (135)
Styrene-co-ethylene-co-propylene-g-glycidyl methacrylate	PP/PET (137)
Styrene-co-ethylene-co-butadiene-co-styrene-g-glycidyl methacrylate	PP/PET (137)
PP-g-monomethyl itaconate	PP/EPDM (139)
PP-g-dimethyl itaconate	PP/EPDM (139)
PP-g-maleic anhydride	PP/EPDM/PA6 (262)
PP-g-acrylic acid	PP/EPDM/PA6 (262)
PP-g-monomethyl itaconate	PP/EPR (163)
PP-g-primary amine	PP/TPU (228)
PP-g-secondary amine	PP/TPU (228)
N,N-m-Phenylene bismaleimide	PP/natural rubber/PE (238)
N,N-m-Phenylene bismaleimide	PP/EPDM/natural rubber (244–245)
Polyoctenamer	PP/PE/natural rubber (254)
Polystyrene-modified natural rubber	PP/natural rubber (288)
PP-g-maleic anhydride	PP/EVA (294)
Hydroxylated EVA	PP/EVA (294)
Ethylene-co-butyl acrylate-co-glycidyl methacrylate	PTT/PE (37)
EPDM-g-maleic anhydride	EPDM/natural rubber (44, 240, 250)
EPDM-g-styrene-co-acrylonitrile	EPDM/SAN (53)
Ethylene-co-octene-g-maleic anhydride	EPDM/TPU (91)
Mercapto-modified EVA	EPDM/NBR (234)
EPDM-g-maleic anhydride	EPDM/PA6,10 (266)
EPDM-g-maleic anhydride	EPDM/PA12,10 (266)
EPDM-g-vinyltriethoxysilane	EPDM/PE (275)
EPDM-g-vinyloxyaminosilane	EPDM/PE (296)
EPR-g-maleic anhydride	EPR/PA6 (57, 60)
EPR-g-MAH + epoxy-modified lignosulfonate	EPR/lignin (172)
Styrene-co-isoprene	Natural rubber/PS (290)

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for more expensive engineering thermoplastics. There is also a growing interest in the use of elastomer-rich thermoplastic olefin blends that contain 60–75% rubber and 40–25% polypropylene for automotive interior applications because they provide the required amount of lower and upper service temperature performance. There is also growing use of beta nucleator functional additive in polyolefin blends, for example, PP/EPR blend. A beta nucleating agent leads to blend with improved impact and ductility.

The second growing trend is the impact modification of polyolefin blends using styrenic block copolymers, which are known to be clear, strong, have low glass transition, compatible with PP, form interpenetrating polymer networks, and very efficient in contrast to maleic anhydride-grafted polyolefins.

The third trend is the growing interest in functionalization of polyolefin blends in their melt by means of reactive extrusion. Particular attention has been paid to blended systems PP/PE, PP/EPR, PE/ethylene–octene copolymer (EOC), PP/EOC, PE/PS, and PP/PS functionalized in melt by reactive extrusion. The major field for application of functionalized polyolefin blends is compatibilization of blends of condensation polymers, where they can be used in place of homopolyolefins.

The fourth trend is spurred by environmental sustainability concerns and the need for increased recyclability and reuse of polyolefin blends. In this regard, there is increasing replacement of PVC by polyolefin–polyolefin blends. There is also an increase in recyclability of EPDM rubber vulcanizates since EPDM is the fastest growing elastomer among synthetic rubber and the most used of nontire rubbers. Also, cryogenically ground rubber tires are being used as fillers for polyolefin blends such as LLDPE/HDPE.

The fifth trend is the use of beta nucleator as opposed to alpha nucleator in PP containing blends such as PP/EPR. The use of beta nucleating agent results in blend with improved impact and ductility

The sixth trend is the growing interest in foams, nonwoven, and elastic materials based on polyolefin blends

The seventh trend is the increasing use of novel processing methods. For example, there is growing use of supercritical fluids (e.g., supercritical carbon dioxide and nitrogen gases) to foam polyolefin blends for density reduction. There is use of ultrasound to, for example, devulcanize cross-linked rubber. There is use of solid-state shear mechanical processing to break the polyolefin blend material into submicron particles to make environment friendly (water-based) polyolefin dispersions. There is use of electrospinning technique to make polyolefin fibers and in particular nanofibers.

In conclusion, the importance of polyolefin blends has increased dramatically in the last couple of decades and this is sure to continue as new polyolefins are made and as new applications are sought for these materials.

NOMENCLATURE

AFM	Atomic force microscopy
BR	Butyl rubber

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Chapter 2

Miscibility and Characteristics of Polyolefin Blends

James L. White[1] and Jinhai Yang[1]

2.1 INTRODUCTION

It is our purpose here to summarize the characteristics of blends of polyolefins. We consider both blends of polyolefins with other polyolefins and with nonpolyolefins including polyamides and polystyrenes. In the case of interpolyolefin blends, our primary concern is with miscibility. In the case of blends of polyolefins with nonpolyolefins, the blends are all immiscible and our concern is with phase morphology. We also consider three component blend systems where the third component is a surfactant or compatibilizing agent, which collects at the interface.

2.1.1 Polyolefins

Olefins are a group of unsaturated hydrocarbons of the general formula C_nH_{2n}. The polymers of olefins are known as polyolefins. Commercial polyolefins mainly include homopolymers of the olefin monomers: ethylene, propylene, butene-1, isobutene, and 4-methylpentene-1.

These homopolymers have structure units as shown in Fig. 2.1, where the asterisk indicates asymmetric carbon atoms. Thus, polypropylene (PP), poly (butene-1) (PB1), and poly(4-methylpentene-1) (P4MP1) have different tactic forms. The most important commercial polyolefins are polyethylene, polyisobutene, and the isotactic forms, that is, iPP, iPB1, and iP4MP1. Polyisobutene was first polymerized by the IG Farbenindustries (BASF) in the late 1920s. Polyethylene was first polymerized by ICI in the late 1930s in a branched form (1). Linear polyethylene

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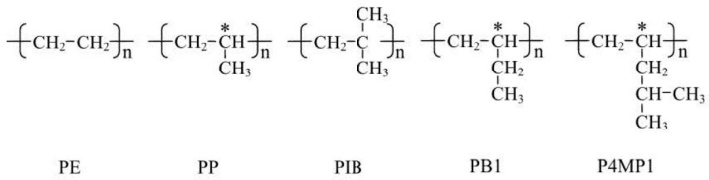

Figure 2.1 Structure units of polyolefins.

was developed by Ziegler and coworkers (2) and by Phillips Petroleum (3) in the 1950s. The other isotactic polyolefins were polymerized by Natta et al. (4,5) using modified Ziegler catalysts in the 1950s.

It is a very interesting question why only these five types of polyolefins are commercialized, considering that there are many more types of olefin monomers. This is largely associated with their crystalline melting temperatures. Polyethylene, polypropylene, and polybutene-1 have reasonable melting temperatures, in particular, 135, 165, and 120°C, respectively. However, the melting temperatures decrease greatly with increase of the pendant group length in the isotactic polymers, for example, polypropylene (165°C), polybutene-1 (120°C), polypentene-1 (70°C), polyhexylene-1 (−55°C), polyheptylene-1 (−40°C), and polyoctylene-1 (−38°C) (6,7). Introducing methyl groups onto the side group raises the melting temperatures, for example, poly(3-methylbutene-1) (300°C), poly(4-methylpentene-1) (235°C) (7). Polyisobutylene, which crystallizes with difficulty has become a significant synthetic rubber.

In addition to the homopolymers, there are various polyolefin copolymers. Linear low density polyethylene (LLDPE) is probably the largest. This involves ethylene copolymerized variously with butene-1, hexene-1, octene-1, and 4-methylpentene-1, and so on. Here the second comonomer content is around 5 mol%. In the 1990s, Exxon (8) and Dow Chemical (9,10) began to make polyolefin copolymers using new generation of Ziegler–Natta catalysts called metallocene catalysts. Polymers were also made with high comonomer contents and the density was as low as 0.86 g cc^{-1} (compared to 0.83 g cc^{-1} for amorphous polyolefins). It should be noted that these are random copolymers. Recently, Dow Chemical (11) made polyolefin block copolymers using "chain shuttling polymerization." These block copolymers display melting temperature around 40°C higher than those of random copolymers of equivalent density. Ethylene–propylene copolymers, which usually contain roughly 50–75 mol% of ethylene, are also important polyolefin copolymers. These comonomers are elastomers and are defined as ethylene–propylene copolymer (EPM) or ethylene–propylene rubber. Terpolymers are commercially more important than EPM and are produced by polymerizing ethylene and propylene together with a diolefin, which are called ethylene–propylene diene terpolymer (EPDM).

Since the late 1990s, another group of polyolefins, cyclopolyolefins, were developed (12,13). They are homo- or copolymers formed by the polymerization

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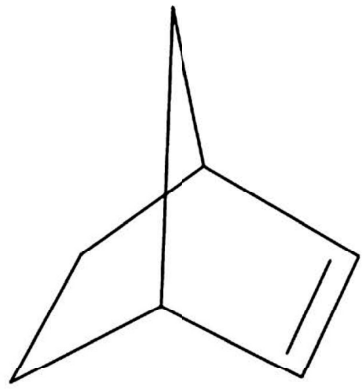

Figure 2.2 Norbornene form (I).

of norbornene derivatives of form (I) shown in Fig. 2.2. The bridged ring structure of norbornene does not readily fit into crystalline lattices, which together with comonomers make the resins completely amorphous with high transparency and high glass transition temperature, for example, 200°C with 60 mol% of norbornene (14). They are used in competition with polymers such as polycarbonate and polymethylmethacrylate for applications such as optical discs and lenses.

2.1.2 Blends

Though more and more polymers have been synthesized since 1930s, however, they could not satisfy the fast growing millions of applications especially in electric, architecture, and automobile after 1960s. Thus, both blends and composites are compounded greatly to compensate the gap. So far, compounding is the most fast, economic, and efficient material development method for new applications. At present, about 36% of the synthetic resins are used in blends and about 39% in compounds with particle and fibers (15). Polymer blends date to the nineteenth century. In 1846, Parkes patented the first polymer blends of *cis*-1,4 polyisoprene (natural rubber) and trans-1,4 polyisoprene (gutta percha) (16). The modern era of polymer blending is thought to begin with the development of high impact polystyrene (HIPS) (17) and poly(acrylonitrile–butadiene–styrene) terpolymer (ABS) (18–21) in the 1950s and polyphenylene ether (PPE)/ polystyrene (PS) blends by General Electric (22) in the 1960s.

Polymer blends can be divided into two groups: miscible and immiscible blends. Miscible blends are homogeneous and stable. Their properties tend to be intermediate. However, they are relatively few. Most polymer blends are immiscible. Their properties are strongly affected by their phase morphologies, which are decided by their viscosity, interfacial tension, and processing methods. In this review we will describe polyolefin blends. Many of these blends involve polar polymers with polyolefins.

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