

Supercritical carbon dioxide as a green solvent for processing polymer melts: Processing aspects and applications

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Abstract

Supercritical carbon dioxide (CO₂) is well established for use as a processing solvent in polymer applications such as polymer modification, formation of polymer composites, polymer blending, microcellular foaming, particle production and polymerization. Its gas-like diffusivity and liquid-like density in the supercritical phase allow replacing conventional, often noxious, solvents with supercritical CO₂. Though only a few polymers are soluble in supercritical CO₂, it is quite soluble in many molten polymers. CO₂ dissolution in a polymer has been interpreted physically but FT-IR studies lead to an explanation in terms of weak interactions between basic and acidic sites. Various experimental methods and equations of state are available to measure or predict the solubility of CO₂. Dissolved CO₂ causes a considerable reduction in the viscosity of molten polymer, a very important property for the applications stated above. CO₂ mainly acts as a plasticizer or solvent when contacted with a polymer. Gas solubility and viscosity reduction can be predicted theoretically from pure-component properties. In this review, experimental and theoretical studies of solubility and viscosity of several polymer melts are discussed in detail. Detailed attention is also given to recently reported applications along with aspects related to polymer processing.

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Keywords: Supercritical CO₂; Solubility; Equation of state; Viscosity; Polymer modification; Blending; Composites; Foaming; Particle production; Polymerization

Abbreviations used: ASES, aerosol solvent extraction system; FT-IR, Fourier transform infrared; GAS, gas antisolvent crystallization; M–B, Martire and Boehm; MLSR, magnetically levitated sphere rheometer; MSB, magnetic suspension balance; New-1, new mixing rule; PCA, precipitation by compressed antisolvent; PGSS, particles from gas-saturated solutions; P–V, Panayiotou and Vera; P–R, Peng and Robinson; RESS, rapid expansion of supercritical solutions; SAFT, statistical association fluid theory; SAS, supercritical antisolvent precipitation; SEDS, solution enhanced dispersion by supercritical fluid; S–L, Sanchez and Lacombe; vdW1, van der Waals one parameter mixing rule; vdW2, van der Waals and two parameters mixing rule; WLF, Williams–Landel–Ferry; CA, cellulose acetate; EEA, ethylene–ethylacrylate copolymer; EVOH, ethylene–vinyl alcohol copolymer; HDPE, high density polyethylene; LDPE, low density polyethylene; PA, polyamide; PBMA, poly(butyl methacrylate); PBS, poly(butylene succinate); PCL, poly-ε-caprolactone; PDMS, poly(dimethyl siloxane); PE, polyethylene; PEG, poly(ethylene glycol); PEO, poly(ethylene oxide); PET, poly(ethylene terephthalate); PLA, polylactide; P_{D,L}L, poly(DL-lactic acid); PLGA, poly(lactide-co-glycolide); PMMA, poly(methyl methacrylate); PP, polypropylene; PPG, poly(propylene glycol); PPO, poly(2,6-dimethyl-1,4-phenylene ether); PS, polystyrene; PTET, poly(trimethylene terephthalate); PTFE, poly(tetrafluoroethylene); PVAc, poly(vinyl acetate); PVDF, poly(vinylidene fluoride); PVME, poly(vinyl methyl ether); PVOH, poly(vinyl alcohol); TiO₂, titanium dioxide.

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Nomenclature

A, B	Doolittle's equation constants	r	number of lattice sites
a, b	P–R EOS constants	R	gas constant
a_c	concentration-dependent shift factor	V	volume
a_p	pressure-dependent shift factor	w	weight fraction
a^{res}	Helmholtz energy (residual)	x	mole fraction
a_T	temperature-dependent shift factor	δ	interaction parameter
f	free volume fraction	ϵ	characteristic energy
i, j	components	ϕ	volume fraction
l, k	adjustable parameters (P–R EOS)	η_0	viscosity of polymer solution
M	number average molecular weight	$\eta_{0,p}$	viscosity of pure polymer melt
P_c	critical pressure	ρ	density
T_c	critical temperature	v	specific volume
T_g	glass transition temperature	$*$	characteristic parameters
T_m	melting point	\sim	reduced parameters

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1. Introduction

During the past several decades, polymers have become an inseparable part of daily life. In view of their

importance in various applications, increasing attention is being given, not only to synthesis, but also to polymer processing. Processed polymers are used in various applications in various forms, for examples in the paint

or drug industries as particles, in separation applications as porous membranes etc. In various traditional methods of polymer processing, environmentally hazardous volatile organic solvents (VOCs) and chlorofluorocarbons (CFCs) are generally used. Due to the enormous increment of hazardous solvents emissions and generation of aqueous waste streams, chemists and chemical engineers are seeking new and cleaner methods for the processing of polymers. One such method is the use of supercritical fluids as processing solvents or plasticizers. Today, use of supercritical fluids in polymer applications is pursued not only in research laboratories but also has recently been adopted on a commercial scale. Several companies e.g. Thar Technologies, Micell, Trexel, DuPont and Ferro Corporations are already realizing the potential of supercritical fluids in applications.

A supercritical fluid is defined as a substance for which both pressure and temperature are above the critical values (Fig. 1). The special combination of gas-like viscosity and liquid-like density of a supercritical fluid makes it an excellent solvent for various applications. The density of supercritical fluids can be tuned easily by small changes in pressure within the critical region. Supercritical fluids have been used successfully as solvents, or antisolvents or plasticizers in polymer processings: e.g. polymer modification, polymer composites, polymer blending, microcellular foaming, and particle production, and in polymer synthesis [1–5]. Moreover, improved product quality is an important factor in the selection of supercritical fluids, as compared to conventional organic solvents [1–5].

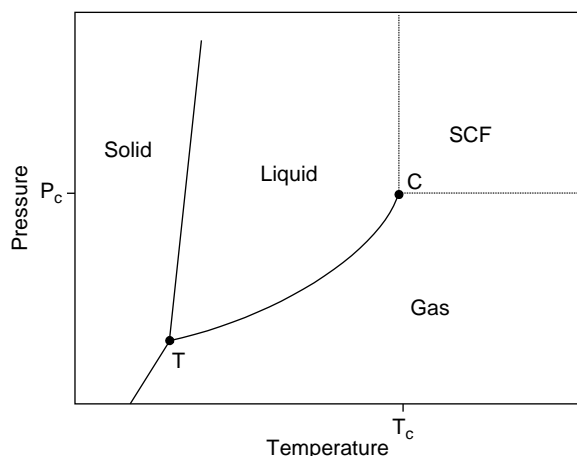


Fig. 1. P–T phase diagram of fluid: (1) T, triple point; (2) C, critical point.

Supercritical carbon dioxide is most often used in these applications. It is a clean and versatile solvent and a promising alternative to noxious organic solvents and chlorofluorocarbons. It has attracted particular attention as a supercritical fluid in the synthesis as well as processing areas for polymers owing to its attractive physical properties. It is non-toxic, non-flammable, chemically inert and inexpensive. Though it is abundant in the atmosphere, a large amount is also available as a by-product from NH_3 , H_2 and ethanol production. Its supercritical conditions are easily attained ($T_c=304\text{ K}$, $P_c=7.38\text{ Mpa}$) and it can be removed from a system by simple depressurization. Moreover, many polymers become highly swollen and plasticized in the presence of CO_2 , allowing processing at low temperatures. The use of supercritical CO_2 does not create a problem with respect to the greenhouse effect as it is recovered during processing.

Supercritical CO_2 is a good solvent for many non-polar (and some polar) low molecular weight compounds [6] and a few polymers, such as certain amorphous fluoropolymers and silicones [4,7–10]; but it is generally a very poor solvent for high molecular weight polymers under readily achievable conditions. However, the solubility of supercritical CO_2 in many polymers is substantial. Its solubility depends on temperature and pressure and also on weak interactions with the chain groups in the polymer. Dissolved CO_2 causes a considerable reduction in the viscosity of molten polymer due to an increase in free volume. Moreover, it alters physical properties of polymers such as density, diffusivity and swollen volume. Therefore, it has tremendous potential as a plasticizer in polymer processing, which is generally carried out at high temperatures.

Much attention has been paid to situations where supercritical CO_2 is dissolved in polymers. The reviews by Cooper [1] and Tomasko et al. [2] give extensive information on various applications of supercritical CO_2 to polymer synthesis and processing. Recently, Kendall et al. [5] have nicely reviewed various polymerizations in supercritical CO_2 . However, detailed information on polymer– CO_2 thermodynamics is not available in the reviews [1,2,5]; and only limited parts of these reviews concern molten polymers, the most likely form for processing. The major motivation for this review is the rapid growth in research on processing of molten polymers with supercritical CO_2 . Accordingly, we focus mainly on that subject.

Scrutiny of the literature reveals the considerable attention that many researchers have given to topics related to polymer melts and CO_2 . Today, the use of

supercritical CO₂ as a solvent can also be seen in the processing of various biodegradable/biocompatible polymers for pharmaceutical and medical applications in the forms of particles and microcellular foam. The low thermal stability of biodegradable polymers and the lack of organic solvents in processing them are the main reasons for the emergence of supercritical CO₂ as a replacement solvent.

This review covers mainly developments in supercritical CO₂-assisted polymer processing over the last two decades. The commercial success of a supercritical-polymer process lies not only in the process design but also in understanding other aspects relevant to the process. Therefore, we give detailed attention to various questions related to processing such as polymer–CO₂ interaction, solubility, and viscosity reduction. The discussion should help to provide a more complete picture of supercritical technology applicable to molten polymers. The applications mainly involve polymer modifications, polymer blending, polymer composites, microcellular foaming and particle production. Moreover, CO₂ also plays the role of a plasticizer in many polymerizations where the viscosity of the synthesized polymer is reduced by dissolved CO₂ and, consequently, conversion is increased by enhanced mass transfer [5]. Therefore, we also discuss the polymer synthesis in supercritical CO₂ but give only the most recent updates.

2. Solubility of supercritical CO₂ in polymers

Useful information on the solubility of subcritical and supercritical CO₂ in polymers above their glass transition temperature (T_g) or melting point (T_m) is widely dispersed in the literature. Solubility data obtained at various temperatures and pressures provide useful criteria to determine requisite processing conditions. One example is the requirement of a single-phase solution in viscosity measurements, blending and microcellular foaming. To avoid phase separation in these applications, the concentration of dissolved CO₂ must be kept below the solubility limit. Unfortunately, only limited data on the solubility of supercritical CO₂ in molten polymers are available despite its importance. Irrespective of processing conditions, the quantity of CO₂ dissolved in a polymer depends on the constituent chain groups; solubility differences can be explained in terms of specific weak intermolecular interactions between CO₂ and the polymer.

Several studies have been carried out to explore the interactions between polymer and CO₂. The Lewis

acidity of CO₂ is the main contributor to its solubility. In 1975, Pilato et al. [11] suggested that dipole–dipole interaction between CO₂ and the sulfone group of polysulfone is the major reason for the relatively high solubility of CO₂ in this polymer. Later, interactions between CO₂ and carbonyl groups of poly(methyl methacrylate) (PMMA) and cellulose acetate (CA) were determined by Fourier transform infrared (FT-IR) spectroscopy [12]. The results indicated that the carbonyl stretching vibrations for CA and PMMA shift to slightly higher wave numbers with increasing pressure of CO₂. Several silicone polymers with different functional groups in the backbone chains have also been tested with CO₂ [13]. In this case, a decrease in the free volume of silicone polymers due to additional functional groups has a greater effect on the solubility than differences in gas–polymer interactions. Later, Briscoe and Kelly [14,15] used an optical high-pressure cell and FT-IR spectroscopy to relate polymer swelling with interaction between CO₂ and polyurethane elastomer. These studies revealed a spectral shift associated with hydrogen bonding. A similar trend in swelling and spectroscopic shift data was observed, with limiting values reaching a plateau at high pressures. The plateau was attributed to the hydrostatic component of the gas pressure, which suppresses further uptake of gas.

These studies provided no spectroscopic evidence of Lewis acid–base interaction between CO₂ and polymer. The bending mode of CO₂, unnoticed in these studies, which is much more sensitive to Lewis acid–base interaction, was used by Kazarian et al. [16–18] to provide the evidence for such interactions. A splitting of the bending mode was observed with polymers having carbonyl groups. Moreover, the width of the absorption band of the CO₂ bending mode was used to obtain a rough estimate of the CO₂ solubility. Recently, detailed FT-IR studies of the interaction of CO₂ with poly(ethylene terephthalate) (PET), poly(dimethylsiloxane) (PDMS), poly(ethylene glycol) (PEG), polystyrene (PS)/poly(vinyl methyl ether) (PVME) and poly(ethylene oxide) (PEO)/PMMA have been reported [19–22]. Limited research has been carried out to obtain a quantitative relation between wavenumber shift and the solubility of CO₂.

2.1. Solubility experiments

In the past, little attention was given to measurement of the solubility of CO₂ in molten polymers at elevated pressures owing to a lack of the understanding of the role of supercritical CO₂ in polymer processing. More

than fifty years ago, solubility data were obtained on CO₂ at moderate pressures in PS, polyethylene (PE), and polypropylene (PP) melts [23–25]. In these measurements, the solubility cell was constructed as a hollow cylindrical rod in which a pre-molded polymer sample was exposed to gas at different pressures. A fall in pressure with time was used to determine the diffusion coefficient, and the solubility was calculated from the pressure difference, temperature, system volume, and sample weight. Later, sorption studies of CO₂ in poly(ethylene terephthalate) (PET) system at temperatures above the glass transition temperature were reported, but also only at low pressures [26].

Fortunately in the last decade, various methods for the solubility measurements at elevated temperatures and pressures have been published. These are applied to both solid and molten polymers. An overview of the various methods is given in Table 1 [27–42], and a brief discussion is given here of the more commonly used methods.

2.1.1. Phase separation method

In this method, a molten polymer is exposed to the desired gas pressure in an autoclave. After a few hours, samples are taken from the two phases, a polymer-rich phase and a CO₂-rich phase, of the polymer/CO₂ system at equilibrium. The amount of CO₂ in the polymer-rich phase determines the solubility of CO₂ in

the polymer. This method is mainly applicable to low viscosity polymers where mixing is relatively easy.

2.1.2. Pressure decay method

In a closed system containing CO₂ and a polymer, the sorption of CO₂ in the polymer causes a reduction in pressure with respect to time until equilibrium is reached: i.e. when there is no further reduction in pressure. The pressure, the temperature, the volume (empty) of the system, and the volume occupied by the sample are used to calculate the amount of CO₂ present initially. In this method, the system volume is always selected such that even a very small reduction in the amount of CO₂ in the gas phase will produce a marked pressure reduction. However, the swelling of the polymer has to be taken into account as it determines the phase volumes. The theoretical Sanchez Lacombe (S–L) equation of state (EOS), discussed in detail in Section 2.2.1, is generally used to estimate the swelling of polymer due to dissolved CO₂. The pressure, temperature, and swelling are used to calculate the amount of free CO₂ present. The difference between the initial and final amounts of CO₂ gives the amount of CO₂ dissolved in the polymer.

2.1.3. Gravimetric method

In the gravimetric method, the weight difference between a CO₂-free polymer sample and the CO₂-sorbed

Table 1
Sorption studies of polymer/supercritical CO₂ systems

Method	Polymers	Pressure (MPa)	Temperature (K)	Upper experimental limit	Reference
Phase separation	PEG 400, 600, 1000	1–29	313, 323	373 K, 35 MPa	[28]
Phase separation	PDMS	1–26	323, 353, 373	N.R.	[29]
Phase separation	PEG 1500, 4000, 8000, 35000	2–30	316–373	N.R.	[32]
Phase separation	PEG 200, 400, 600	3–26	313–348	423 K, 50 MPa	[33]
Phase separation	PEG 200, 1500, 4000, 8000	5–30	323–393	423 K, 50 MPa	[34]
Pressure decay	PMMA, PS	13.78	293, 473	N.R.	[27]
Pressure decay	PS	1–20	373, 453	N.R.	[30]
Pressure decay	PP, HDPE	1–17	433, 453, 473	N.R.	[31]
Piezoelectric-quartz sorption	PVAc, PBMA	1–10	313, 333, 353	N.R.	[35]
Chromatographic	PMMA	1.5–9	236–453	N.R., 9 MPa	[36]
Chromatographic	PDMS	1.5–10	308–393	N.R.	[37]
Gravimetric	PBS, PBSA	1–20	308–393	523 K, 35 MPa	[38]
Gravimetric	PVAc	1–17.5	313–373	523 K, 35 MPa	[39]
Gravimetric	PS	1–20	373–473	523 K, 35 MPa	[39]
Gravimetric	PPO, PPO/PS	1–20	373, 427, 473	523 K, 35 MPa	[40]
Gravimetric	LDPE/TiO ₂	1–15	423, 448, 473	N.R.	[41]
Gravimetric	LDPE, HDPE, EEA, PS	1–12	423–473	523 K, 35 MPa	[42]

N.R., not reported.

polymer sample is used to calculate the solubility. The method has some advantages over the methods described earlier: need for only a small amount of sample, high sensitivity to small weight changes (using a microbalance), and a short measurement time. A magnetic suspension balance (MSB) apparatus, developed by Kleinrahn and Wagner [43], has been used to determine CO₂ solubilities in several molten polymers. The weight difference is determined by measuring the force required to suspend a sample enclosed in a pressure vessel without having contact with the microbalance. An electronically controlled magnetic suspension coupling transmits the signal to the microbalance. An additional advantage is that the microbalance can be tared and calibrated during measurements. However, the swelling of polymer must be incorporated in the solubility calculations to account for the buoyancy correction. The S–L EOS is generally used to estimate the swelling of polymer by dissolved CO₂.

2.1.4. Chromatographic method

In the chromatographic method [44,45] solubility measurements are carried out with a very thin film (micrometers) of polymer as a stationary phase and CO₂ as a mobile phase. The measurement of the specific retention volume of a tracer determines the CO₂ solubility in the polymer. The major advantage is that the experiments are very fast owing to a very rapid approach to thermodynamic equilibrium of CO₂ with the very thin polymer film.

Considering the importance of polymer swelling in solubility calculations in some of the methods discussed above, it is noteworthy that a recently developed experimental setup [46] is capable of measuring, in situ, the swelling behavior of a polymer melt in contact with high-pressure fluid (e.g. poly (dimethyl siloxane) (PDMS)/CO₂). This arrangement allows optical monitoring of swelling in real-time. The swelling kinetics data can be used for diffusivity calculations, and the equilibrium swelling for solubility calculations. None of the above methods measure solubility under real processing conditions where the residence or contact time is very short. However, the broad applications of extrusion foaming with supercritical carbon dioxide as the foaming agent, have motivated development of a new in-line measurement technique to determine the solubility of gas in a polymer melt during extrusion [47]. In this method, dynamic solubility data are generated by observing the onset of bubble formation/dissolution through an

optical window with a microscope-CCD camera system. Measurements using this technique have so far been reported only for low CO₂ pressures [47].

2.2. Theoretical

The theoretical modeling of solubility data is as crucial as experimental measurements for a complete understanding of processes where thermodynamics plays a vital role; and, incidentally, theoretical calculations are inexpensive compared to experiments. Modern thermodynamic EOS theories for polymer/solvent systems, discussed below, have proved indispensable to understanding and predicting polymer/CO₂ solubility properties. In all these theories, phase equilibria of pure components or solutions are determined by equating chemical potentials of a component in coexisting phases.

Apart from the EOS theories, the Henry's law is a useful relation that can be applied to gas-polymer melt solutions at low pressures (up to ca. 2 MPa) [24,25]. Above a critical gas concentration (specific for each gas-polymer melt combination and for each temperature), the gas sorption isotherm begins to deviate significantly from Henry's law. The deviation can be modeled empirically by a Langmuir type isotherm, but only to moderate pressures [48]. Extrapolation to higher pressures using parameters determined at lower pressure produces increasing inaccuracy in data modeling. Furthermore, the original Flory-Huggins lattice theory [49] generally used for polymer solutions cannot be applied over a wide range of concentrations for CO₂ and molten polymer systems because it does not account for the free volume of the polymer, which is an essential parameter in predicting the dependence of solubility on pressure, temperature, and solution composition [50]. Thus, early predictions of phase equilibria of CO₂ and molten polymer systems were only of limited value.

In the last thirty years, the introduction of EOS theories has brought about a revolution in thermodynamic studies of polymer/CO₂ phase equilibrium, due to the fact that the fundamental thermodynamic functions, e.g. free energy, can easily be obtained from an EOS. An appropriate EOS can be used to describe the phase behavior of polymeric materials, supercritical fluids and their mixtures over a wide range of densities. The commonly used EOS models for polymer/CO₂ systems are conveniently considered in three categories based on lattice theory, cubic EOSs and off-lattice theory.

2.2.1. Lattice fluid theory

In a lattice theory the polymer molecules are ordered according to a lattice structure. The change in volume due to the presence of holes on the lattice is the basic idea behind the theory. It does not require separate parameters to account for the flexibility of the molecule and can be used to calculate the heat and volume of mixing, lower critical solution temperature, and enthalpic and entropic components of the chemical potential. The theory reduces to the Flory-Huggins theory at low temperatures.

Various EOSs based on the lattice model approach have been applied to polymer melt/CO₂ solutions. The EOSs are represented in terms of dimensionless reduced variables such as reduced pressure \tilde{P} , reduced temperature \tilde{T} , and reduced density $\tilde{\rho}$ or reduced specific volume \tilde{v} of the mixture. The reduced variable is defined as the ratio of the variable to its characteristic parameter. The characteristic parameters of the mixture are determined from the characteristic parameters of the pure components. The EOSs of the pure components are used to determine the characteristic parameters, P^* , T^* , and ρ^* or v^* , of the pure components from pressure–volume–temperature (PVT) properties.

An EOS based on a well-defined statistical mechanical model was first proposed by Sanchez and Lacombe [51,52]. A detailed description of several versions of the S–L EOS model, which extends the basic Flory-Huggins theory, can be found in the literature [53–55]. This is the most commonly used EOS model. The S–L EOS is written as

$$\tilde{P} = -\tilde{\rho}^2 - \tilde{T}[\ln(1 - \tilde{\rho}) + (1 - 1/r)\tilde{\rho}] \quad (1)$$

$$\tilde{P} = P/P^*, \quad \tilde{\rho} = \rho/\rho^*, \quad \tilde{T} = T/T^* \quad (2)$$

$$r = MP^*/RT^*\rho^* \quad (3)$$

where r is the number of lattice sites occupied by a molecule with molar mass M and R is the gas constant. The solubility data are predicted by curve-fitting to experimental data using an adjustable binary interaction parameter, δ_{ij} , which is introduced into the equation for P^* of the mixture.

$$P^* = \sum_i \sum_j \phi_i \phi_j P_{ij}^* \quad (4)$$

$$P_{ij}^* = (1 - \delta_{ij})(P_i^* P_j^*)^{0.5} \quad (5)$$

where ϕ_i and ϕ_j are the volume fractions of the components in the mixture.

Later, the composition-dependent lattice volume concept was modified by Panayiotou and Vera (P–V) by fixing the value of the lattice volume [56]. The result is a relatively simple model compared to the S–L model. In the P–V model the adjustable binary interaction parameter is introduced in terms of the characteristic energy

$$\epsilon^* = RT^* \quad (6)$$

Extending the Flory-Huggins and S–L theories, Martire and Boehm (M–B) [57] developed a model to study phase equilibria. Their model uses the Helmholtz free energy rather than Gibbs free energy. The model relates the composition of the condensed phase directly to the temperature and the density of pure gas. Recently, Kumar et al. [58] formulated an EOS for multicomponent mixtures based on the P–V model. Unlike the P–V EOS, it contains two extra terms accounting for the non-random distribution of molecule segments. This EOS has been applied successfully to poly(vinyl acetate) (PVAc)/CO₂ and to poly(butyl methacrylate) (PBMA)/CO₂ at high temperatures and pressures [35].

2.2.2. Cubic equations of state

The ideal gas law is an approximation or idealization of the behavior of gases that becomes asymptotically correct at low densities. Attempts have been made to accurately represent the non-ideality of gases using various cubic EOSs, and some cubic EOSs have recently been extended to describe the phase behavior of polymer–solvent mixtures [59–62]. However, the applications of these cubic EOSs are mostly limited to the description of phase behavior at low pressures.

Among the cubic EOSs, the Peng and Robinson (P–R) EOS [63] was recently used for correlating high-pressure gas solubilities in molten polymers. Its capability was tested for experimental data by using different mixing rules. Conventional van der Waals (one parameter-vdW1 and two parameters-vdW2) fluid mixing rules and a new mixing rule (New-1) are used in the P–R EOS [64]. The new mixing rule is derived on the assumption that the excess Helmholtz free energy from a two-parameter cubic EOS is zero at infinite pressure [62]. The P–R EOS with the three mixing rules is given by

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b) + b(v-b)} \quad (7)$$

$$b_{ij} = \frac{b_i + b_j}{2}(1 - l_{ij}) \quad (8)$$

$$\begin{aligned} \text{vdW1} - a &= \sum \sum x_i x_j a_{ij}, & b &= \sum x_i b_i, \\ a_{ij} &= \sqrt{a_i a_j} \frac{(b_i + b_j)/2}{\sqrt{b_i b_j}} (1 - k_{ij}) \end{aligned} \quad (9)$$

$$\begin{aligned} \text{vdW2} - a &= \sum \sum x_i x_j a_{ij}, \\ b &= \sum \sum x_i x_j b_{ij}, \\ a_{ij} &= \sqrt{a_i a_j} \frac{(b_i + b_j)/2}{\sqrt{b_i b_j}} (1 - k_{ij}) \end{aligned} \quad (10)$$

$$\begin{aligned} \text{New1} - a &= \sum \sum x_i x_j a_{ij}, \\ a_{ij} &= \sqrt{a_i a_j} \frac{(b_i + b_j)/2}{\sqrt{b_i b_j}} (1 - k_{ij}), \\ \frac{a}{b} &= \sum x_i \frac{a_i}{b_i} \end{aligned} \quad (11)$$

where x_i , x_j are mole fractions, and l_{ij} and k_{ij} are adjustable parameters. In this EOS, the parameters a and b for CO_2 are calculated from its critical properties, While for polymers, the PVT data are regressed. The new mixing rule could fit experimental data with only one adjustable parameter k_{ij} , comparable with the conventional two-parameter mixing rule [64].

2.2.3. Off-lattice theory

An off-lattice theory is based on the fact that real fluids exist in a continuous space (free space) rather than on a lattice. The theory accounts the effect of density on rotational and vibrational motions, in addition to translational degrees of freedom, and includes a pairwise intermolecular interaction energy that is a sensitive function of the intermolecular distance. The statistical association fluid theory (SAFT) is an EOS based on off-lattice theory [65,66]. The approach of the SAFT is to use a reference fluid that incorporates both chain length (molecular size and shape) and molecular association instead of the hard-sphere reference fluid used in most engineering EOSs. The SAFT EOS is defined in terms of the residual Helmholtz energy a^{res} per mole

$$a^{\text{res}} = a^{\text{total}} - a^{\text{ideal}} \quad (12)$$

a^{res} is represented by a sum of three intermolecular interactions: segment–segment interactions, covalent chain-forming bonds among segments and site–site

interactions such as hydrogen bond association, i.e.

$$a^{\text{res}} = a^{\text{seg}} + a^{\text{chain}} + a^{\text{assoc}} \quad (13)$$

The SAFT EOS is applicable to many real fluids including polymers and polymer solutions [67]. Recently, the PEG/ CO_2 system, at elevated pressure, was successfully modeled by the SAFT EOS [34].

Table 2
Theoretical models applied to molten polymer/ CO_2 systems

Polymers	Pressure (MPa)	Temperature (K)	Model see footnotes	Reference
PMMA, PS	13.78	293, 473	a	[27]
PEG 400, 600, 1000	1–29	313, 323	b	[28]
PDMS	1–26	323, 353, 373	a,b	[29]
PS	1–20	373, 413, 453	a	[30]
PP, HDPE	1–17	433, 453, 473	a	[31]
PEG 200, 400, 600	3–26	313–348	a	[33]
PEG 200, 1500, 4000, 8000	5–30	323–393	c	[34]
PVAc, PBMA	1–10	313, 333, 353	a,d	[35]
PMMA	1.5–9	236–453	a,b,e	[36]
PDMS	1.5–10	308–393	a,e	[37]
PBS, PBMA	1–20	323–453	a	[38]
PVAc	1–17.5	313–373	a	[39]
PS	1–20	373–473	a	[39]
PPO, PPO/PS	1–20	373, 427, 473	a	[40]
LDPE/ TiO ₂	1–15	423, 448, 473	a	[41]
LDPE, HDPE, EEA, PS	1–12	423–473	a	[42]
PVAc	3–8.8	333	f	[64]
PVAc	2–7.9	353	f	[64]
PBMA	0.7–5.5	353	f	[64]
PS	7.3–20	413	f	[64]
PS	2.5–17	453	f	[64]
PVAc	2–7.1	313	g	[70]
PVAc	3–8.8	333	g	[70]
PVAc	2–7.9	353	g	[70]
PBMA	0.7–5.5	353	g	[70]
PS	7.3–20	413	g	[70]
PS	2.5–17	453	g	[70]

^a S–L EOS.

^b P–V EOS.

^c SAFT.

^d Kumar EOS.

^e M–B EOS.

^f PR EOS with vdW1, vdW2, and New-1.

^g EOS (by Li and Hu), the SAFT, the PR EOS.

Liu and Hu [68,69] developed a simplified EOS for chainlike molecules, i.e. polymer, by combining the hard-sphere-chain-fluid equation with a square-well perturbation term. The EOS was further extended to correlate CO₂ solubilities in molten polymers by introducing two adjustable binary interaction parameters: one to adjust the interaction energy and the other to adjust the collision diameter between segments in mixtures [70]. This EOS showed comparable predictive power to the SAFT and the P–R EOS for the several polymers.

All the EOSs discussed above have been applied successfully to various molten polymer–CO₂ systems (Table 2). Lattice theory based EOSs are used more than the off-lattice based EOSs. The reason may be the simpler physical representation as compared to the off-lattice treatments. Among the lattice theory EOSs, the S–L EOS has most frequently been used. However, the P–V EOS shows better predictive capability than the S–L EOS for the molten PDMS/CO₂ system [29]. The P–V EOS is superior because it predicts a critical temperature of CO₂ closer to the actual value. The P–R EOS with the new mixing rule can also be a good choice for modeling phase equilibria because of its simplicity compared to the statistical mechanics-based models (lattice and off-lattice). Since, the EOSs discussed here have not been individually applied to every molten polymer–CO₂ system study reported in the literature, it is difficult to judge their thermodynamic modeling capabilities at this stage. Clearly much more experimental data are needed.

3. Viscosity reduction

High viscosity is a major obstacle in processing high molecular weight polymers. To overcome this obstacle, one option is processing at high temperatures since viscosity decreases with increasing temperature. However, at elevated temperatures the degradation of polymers is an important concern. The use of organic solvents can overcome this problem as the viscosity can be reduced at a low temperature. Nevertheless, problems associated with environmental concerns, separation and recovery of solvent, and the reactive nature of solvent, are always present.

Supercritical CO₂ is a good replacement for organic solvents in handling highly viscous polymer melts. The dissolution of CO₂ in a polymer causes its plasticization even at low temperatures. The plasticization is evidenced by a decrease in the glass transition temperature or melting point of the polymer [71–76] which in turn results in a reduction in the viscosity [77].

Thus, the use of CO₂ allows processing of polymers at low temperatures and polymer degradation is avoided. In view of these advantages, increased attention is being given to experimental and theoretical rheological studies of polymer/CO₂ solutions.

3.1. Experimental

Prevention of gas leakage at elevated pressures, formation of a single-phase solution and prevention of separation of a single phase into two phases are the major challenges to viscosity measurements in polymer/gas solutions. To avoid these problems, a capillary extrusion rheometer was modified for high-pressure rheological measurements of PDMS melts [77]. In this rheometer, a sealed loading apparatus at the top of the rheometer allows the transfer of a sample pre-equilibrated (with gas) in a high-pressure vessel. Further, a backpressure assembly at the exit of the capillary keeps the pressure above the value required to prevent phase separation. The viscosity is determined by the pressure drop across the capillary i.e. the upstream pressure determined from the load cell less the downstream pressure measured by the backpressure transducer. Later, the same high-pressure rheometer was used to measure the effect of CO₂ concentration on the viscosity of PS [78]. Substantial viscosity reductions were found for PS and PDMS melts in the presence of dissolved CO₂.

For the similar system, PS/CO₂, Lee et al. [79,80] performed rheological measurements using a capillary die. In their setup, a static mixer was placed at the exit of an extruder to provide extra mixing. The polymer viscosity was found to decrease with increasing concentration of CO₂ but increased with pressure at high pressures. The compression of the polymer melt at high pressures, the hydraulic pressure effect, is responsible for increased viscosity. Lee et al. [81,82] also published rheological data on PE and PE/PS blends in the presence of CO₂ using a wedge die instead of the capillary die. The viscosity reduction of the PE/PS blend-CO₂ solution lies between of the values for the binary PS/CO₂ and PE/CO₂ solutions.

An extrusion slit die rheometer with a static mixer is another type of rheometer suitable for high-pressure rheological measurements. This type of rheometer has been used for CO₂ solutions in several polymers, polymer blends, and polymer composites including biodegradable polymers: i.e. PS, PMMA, low density PE (LDPE), poly(vinylidene fluoride) (PVDF), linear and branched poly(butylene succinate) (PBS), PE/silicone nitride, PE/glass-beads, acrylonitrile/methacrylate

(AN/MA) copolymer, and PP [83–91]. Maximum viscosity reductions as high as 80% for PMMA/CO₂ and PS/CO₂ have been reported, depending on processing conditions. For PP it was observed that the reduction was greater at low shear rates. This may be explained by the fact that supercritical CO₂ acts as a diluent when the entanglement density of the polymer is not effectively reduced by shear stress.

In the pressure driven devices discussed above, a large pressure drop over a die limits the amount of supercritical CO₂ used in the measurements since, phase separation may occur if the amount of CO₂ dissolved is above the solubility limit. Thus, such devices are most useful when the amount of dissolved CO₂ is far below saturation. This limitation can be overcome by using drag-driven or rotational devices where pressure is constant during measurements and measurements can be carried out at or near saturation concentrations of CO₂.

Recently, a magnetically levitated sphere rheometer (MLSR) [92] and rotational viscometer [93], both drag-driven devices, were used to measure viscosities of CO₂ pressurized solutions of PDMS, and poly(propylene glycol) (PPG) and PPG/fumed silica, respectively. The MLSR eliminates a problem of headspace associated with the high-pressure rotational viscometer; but it is suitable only for Newtonian liquids owing to the complex flow field around the sphere in non-Newtonian fluids.

3.2. Theoretical

In general for polymers, viscosity curves (shear viscosity η vs shear rate $\dot{\gamma}$) obtained at different temperatures are usually of similar shape. It is a very common practice in polymer rheology to generate a master curve by shifting or scaling the viscosity data obtained at different temperatures to the viscosity data obtained at a reference temperature. Similarly, viscosity curves obtained at different CO₂ concentrations can be shifted to the curve obtained for pure polymer using a concentration-dependent shift factor (a_c)

$$a_c = \eta_0 / \eta_{0,P} \quad (14)$$

where η_0 is the shear viscosity of a polymer solution and $\eta_{0,P}$ is the shear viscosity of a pure polymer melt. As an example, the master curve generated for PDMS/CO₂ solution at 323.15 K using the concentration-dependent shift factor is shown in Fig. 2 [77]. Similarly, the effect of pressure on the viscosity (an increase in viscosity with an increase in pressure) can be presented in terms of the pressure-dependent shift

factor (a_p). To consider the effect of the temperature, pressure, and concentration together, the respective shift factors are multiplied together ($a = a_T a_c a_p$). To generate a master curve considering all the effects the product of the shift factors is used instead of an individual shift factor.

In order to predict theoretically the effect of dissolved CO₂ on the viscosity of polymer, it is first necessary to understand the underlying mechanisms. Two mechanisms contribute to the viscosity reduction. The first is the dilution of chain entanglements in the melt when supercritical CO₂ is dissolved. The second mechanism involves generation of additional free volume, which increases chain mobility. The viscosity reduction is mostly due to the second mechanism. Extensive theoretical research using the free volume theory has been carried out on viscosity of polymer/CO₂ solutions.

Doolittle's free volume theory [94] has always been used as a basis. The relation between viscosity and free volume, based on the Doolittle's theory, is given by

$$\eta_0 = A \exp(B/f) \quad (15)$$

where A and B are constants and f is the free volume fraction of the polymer. The free volume fraction is the ratio of the volume accessible to the chain motions associated with the liquid flow to the specific volume of the melt. The accessible volume is the difference between the specific volume of the melt and the occupied volume v_o , which is closely associated with

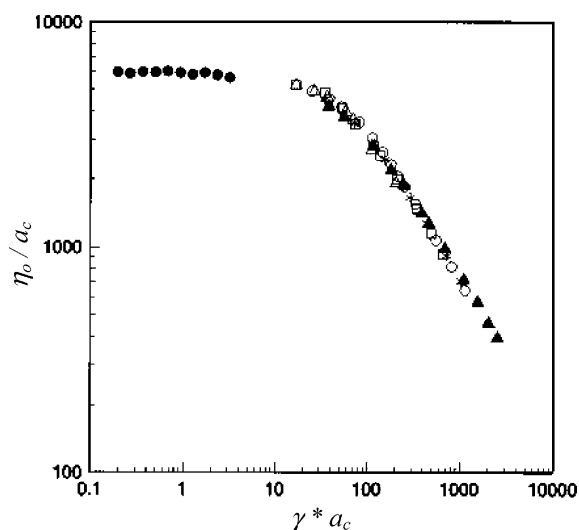


Fig. 2. The master viscosity curve (based on the concentration of CO₂) for the PDMS–CO₂ solution at 323 K [77]. Reproduced from Gerhardt, Gulari and Manke by permission of John Wiley and Sons, NJ, USA.

the hard-core molecular volume of the polymer. For a mixture, the occupied volume is determined by a linear mixing rule

$$v_o = w_{\text{CO}_2} v_o^{\text{CO}_2} + (1 - w_{\text{CO}_2}) v_o^p \quad (16)$$

where w_{CO_2} is the weight fraction of CO_2 dissolved in the polymer.

Gerhardt et al. [95] modified an expression developed by Kelly and Bueche [96], based on Doolittle's free volume theory, to predict shift factors for CO_2 concentration in PDMS. The S–L [51,52] and P–V [56] EOSs were used to calculate the specific volume of the CO_2 -swollen melt from the PVT properties of pure compounds, taking into account the non-ideal mixing. Later, Kwag et al. [97] used the same theory to predict shift factors for PS/ CO_2 . The predicted shift factors with the modified free volume theory [95] were found to be in good agreement with experimental shift factors for both PDMS/ CO_2 and PS/ CO_2 systems, suggesting that the free volume mechanism plays a dominant role in the viscosity reduction caused by dissolved gas.

Later, Lee et al. [81] proposed a new model using the well known generalized Cross-Carreau equation [98] to describe shear thinning of PS– CO_2 solutions, together with Doolittle's free volume theory. Lee et al. expressed the fractional free volume term of the Doolittle theory as a power law series in order to include the effects of temperature, pressure and CO_2 concentration. Viscosity data for pure PS was used to determine the material constants in the Cross-Carreau equation and the modified Doolittle theory.

Using the Williams–Landel–Ferry (WLF) equation [99], directly obtained from Doolittle's free volume theory, and Chow's [100] model, Royer et al. [84,86] recently developed another free volume model. Chow's model was used to determine the glass transition temperature and melting point depression due to dissolved CO_2 which represent an enhancement in the free volume of the polymer. The free volume model was developed in terms of a set of shift-factor equations for pressure and CO_2 concentration analogous to the WLF equation used for temperature. These equations are valid in the range from T_g to $T_g + 373$ K since, the WLF equation is generally applicable in this range, where the increase in free volume with temperature is linear. For a temperature higher than $T_g + 373$ K, Arrhenius type expressions were applied. This free volume model was adopted to generate master curves for PS and PMMA using the WLF analogs and for PP, LDPE and PVDF using the Arrhenius analogs.

Despite the growing number of applications of supercritical CO_2 to polymer melts, experimental rheological data on these systems are still scarce. However, before doing rheological experiments, one should think of the free volume models above, which are based on physical properties and rheological data for pure polymer melts, in order to obtain preliminary estimates of the polymer/ CO_2 solution viscosity.

4. Applications

4.1. Polymer modification

Dissolution of CO_2 in a polymer facilitates diffusion of monomers and catalysts/initiators within the polymer matrix. In this case, CO_2 is the carrier of active chemical species [101] as well as the swelling agent. Accordingly, chemical modification of polymers can be carried out in milder conditions than with standard methods of melt modification in extruders or batch mixers. This is extremely important for polymers, such as poly(tetrafluoroethylene) (PTFE) [102] and PP [103] for which modification in the melt is always accompanied by degradation. Most current research efforts are dedicated to chemical grafting (by radical mechanisms) of monomers onto PP with the general aim of modifying its hydrophilicity. Methyl acrylate [104], 2-hydroxyethyl methacrylate [105], methyl methacrylate [106], styrene [107] and maleic anhydride [108] are reported to be successfully grafted onto PP in CO_2 assisted processes. In all these cases the presence of CO_2 does not modify the radical grafting mechanism [109] but it provides better dispersion of the reactive species in the PP matrix at low processing temperature. In the studies above, a modification in the thermal properties of PP was observed and attributed not only to the grafting of polar groups but to the plasticizing action of CO_2 [110]. This evidences a positive opportunity to modulate the thermal behavior of the modified polymer through the experimental conditions, namely pressure and temperature, at which the modification is carried out.

Addition reactions have also been carried out on polymeric substrates in order to graft chemical groups onto the backbone. Friedmann et al. [111] studied the grafting of isopropyl-isocyanate onto ethylene-vinyl alcohol copolymers (EVOH) concluding that the major advantage of CO_2 consists in the selective dispersion and consequent reaction of the monomer in the amorphous phase of EVOH. As a result the crystallinity of EVOH was fully retained throughout the process. An addition reaction was also used very recently [112] to

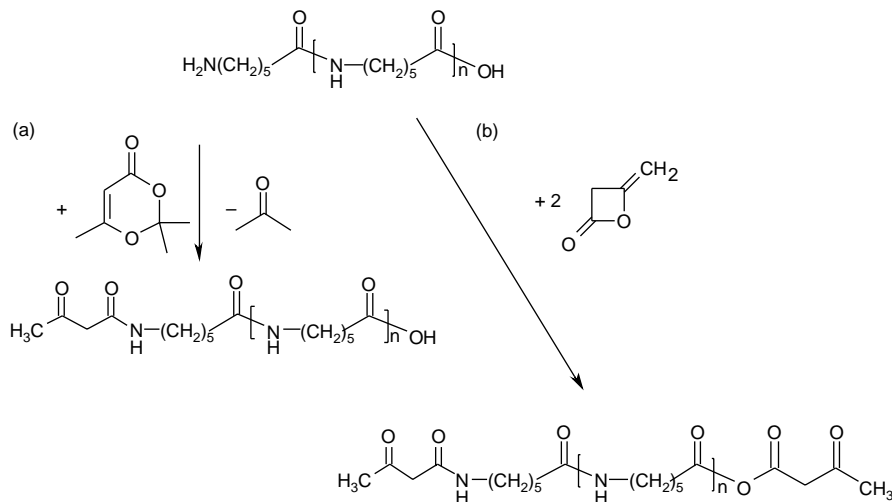
selectively modify the end groups of polyamide-6 (PA) in supercritical CO₂ (Scheme 1). Depending on the reagent used (e.g. diketene or its adduct with acetone), it is possible to selectively modify acid or basic end groups. Again the crucial role of dissolved CO₂ in the swelling of the substrate that favors the chemical reaction must be taken into account.

4.2. Polymer blending

Polymer blending is the process in which two or more immiscible polymers are mixed with each other in a non-reactive or reactive manner. High-power batch mixers and twin screw extruders are the most commonly used apparatus for blending. Blending of immiscible polymers offers scientists and technologists an opportunity to create materials with improved properties, such as impact strength, rigidity etc., compared with the individual polymers. In practice, a blend is usually made of two immiscible polymers. In the non-reactive route, two immiscible polymers (A and B) are mixed in the molten state and form two phases. One phase is disperse (droplets), rich in component B while the other phase is continuous, rich in component A. The viscosity ratio of polymers (B/A) plays an important role in determining the size of the droplets. It is small when the viscosity ratio is close to or less than unity and increases as the viscosity ratio increases [113]. Since, the reduction in viscosity is different for different polymers depending on the amount of CO₂ dissolved under given processing conditions (temperature, pressure and shear rate), the viscosity ratio can be manipulated using CO₂. In the

reactive route, a minor component is synthesized via polymerization into a major component, which acts as a host polymer.

Polymer blends have been prepared in a non-reactive way by batch mixing and extrusion with supercritical CO₂ as a plasticizing agent [27,81,82, 114–119]. The dissolution of supercritical CO₂ in blends leads to decreased shear thinning and a finer dispersion of the minor component. For example, Fig. 3 clearly shows the effect of supercritical CO₂ on the dispersion of the minor phase, PMMA, in a PMMA/PS blend [115]. The greater reduction in viscosity of the minor component allows better momentum transfer from the more viscous major component and causes the minor component to break up into smaller droplets. The effect of CO₂ on a dispersed phase can also be seen through earlier completion of phase inversion compared to blending without CO₂ [116]. Phase inversion is a transformation of high-melting polymer from a disperse phase to a continuous phase. In the presence of CO₂, the length of the extruder required for the phase inversion is shortened because of the decrease in glass transition temperature of the high-melting polymer, and the rest of the extruder length is effectively utilized for reduction of the droplet size of the disperse phase. These studies clearly confirm the possibility of controlling blend morphology (and, therefore, the properties of the blend) in the presence of supercritical CO₂. If foaming of a polymer blend is not desired, venting of CO₂ from the blend is necessary which may cause demixing of the polymers [27]. To prevent demixing, additives such as carbon black, calcium carbonate and nano-clay particles can be used



Scheme 1. End group modification of polyamide 6 with diketene (b) and diketene–acetone adduct (a) [112].

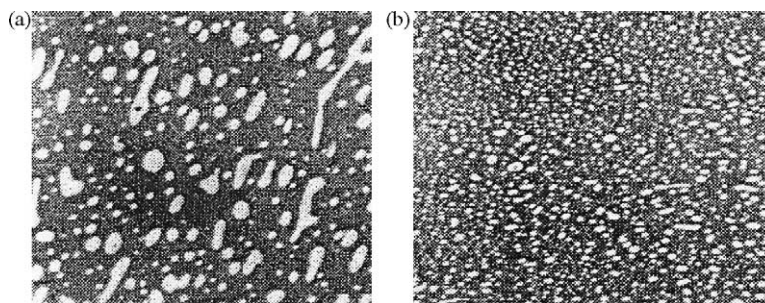


Fig. 3. TEM micrographs of PMMA/PS (25/75) blend: (a) without CO₂; (b) with supercritical CO₂ [27]. Reproduced from Elkovitch, Lee and Tomasko by permission of the Society of Plastics Engineers, USA.

in small amounts (e.g. 3 wt%) during blending; these additives stabilize the interface between the phases after venting of CO₂.

A reactive route for producing polymer blends involves supercritical CO₂-assisted infusion of reagents (monomer and initiator) into and the subsequent polymerization reaction within a host polymer. This route is efficient when monomers and initiator are soluble in supercritical CO₂ and the solubility of CO₂ in the host polymer is high enough to cause it to swell. Swelling enhances the diffusion of reagents and hence, high molecular weight polymer can be synthesized in the host polymer. The main advantage of this route is that the mass uptake of a polymer formed by reaction in the host can be controlled. Variables such as pressure, soaking time and monomer concentration control the total mass uptake of reagents. In this process, polymerization also takes place at the surface of the host polymer. However, the amount of polymer synthesized within the host polymer is always much larger. Several polymer blends with high mass uptake and better distribution of the minor component in the major component have been prepared using the reactive route [120–137]. Among the studies, PS was most frequently selected as a minor component, mainly because of its high modulus.

4.3. Polymer composites

Polymer composites, consisting of inorganic or organic materials incorporated into polymeric matrixes, are the subject of intensive research due to their growing applications in electronic, optical, medicinal and mechanical devices. In the last five years, the same major beneficial effect of CO₂ for polymer blends, namely the improved dispersion of one component in the other, have been exploited by several research groups studying the formation of polymer composites

under supercritical CO₂. The few systems that have been reported so far are (polymeric matrix is reported first): polylactide—(PLA), poly(lactide-co-glycolide)—(PLGA), poly- ϵ -caprolactone—(PCL) or poly(vinyl alcohol)—(PVOH) and calcium hydroxyapatite particles [138], PMMA- or PS- and nylon-6, PP, PET or PE fibers [139]. Other binary combinations are PMMA and clay particles [140], PP and ZnS particles [141], PE and clay particles [142], poly(trimethyleneterephthalate) (PTET) and clay particles [143], and, HDPE and Pd or Rh particles [144].

In some of these examples [139,140] the composite is prepared by in situ polymerization of the polymer matrix in the presence of the other component in the form of particles or fibers. In such cases supercritical CO₂ acts not only as a plasticizer for the synthesized polymer matrix, but also as a carrier facilitating the absorption of the monomer into the fibers or the particles. In other examples [138,141–144] the composite is prepared by blending the matrix with the other component in the presence of supercritical CO₂. In these examples the role of supercritical CO₂ is yet to be systematically investigated. Finally, it must be mentioned that after processing, release of CO₂ often results in foaming, leaving the composite in the form of a porous (micro) material. This is of course very important in supporting the growth of blood vessels and collagen fibers in the matrix of biodegradable polymers [138] or when the final product is intended to be used as catalyst [144].

From the reported studies it is very difficult at the moment to identify a unique molecular mechanism of dispersion of the filler into the polymer matrix. Indeed, the unique morphologies [145] obtained in supercritical CO₂ are reported to be dependent on processing conditions as well as on the interfacial interaction of CO₂ with the surface of the inorganic component, but no systematic study has been published so far.

4.4. Microcellular foaming

Microcellular foaming of polymers, including biodegradable/biocompatible polymers, using supercritical CO₂ as a blowing agent has been touted as a revolutionary invention in the polymer industry [146–151]. Microcellular polymer is defined as having cell sizes of 10 μm or less. Compared with dense polymers, microcellular foams provide a substantial reduction in weight combined with high impact strength, toughness and good fatigue life. Such materials are used in separation media, adsorbents, catalyst supports [152,153], and in other applications. Recently, CO₂, because of its inert nature, has also found use in various medical applications, such as controlled release devices, scaffolds or medical devices where foamed biodegradable or biocompatible polymers are used. The replacement of various traditional blowing agents, such as chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs) and volatile organic components (VOCs), with CO₂ allows working in a clean and safe environment. Moreover, a narrow cell size distribution, easy solvent recovery, good plasticizing ability and high diffusivity are advantages of using supercritical CO₂ in microcellular foaming processes.

Various microcellular polymeric foams have been produced by pressure induced phase separation in batch as well as continuous mode. In either method, the polymer is exposed to CO₂ at the saturation pressure and temperature, which plasticizes the polymer and reduces the apparent glass transition temperature or melting point to the processing, usually near ambient, temperature. On venting the CO₂ by depressurization, thermodynamic instability causes supersaturation of the CO₂ dissolved in the polymer matrix and hence, nucleation of cells occurs. The growth of the cells continues until the polymer vitrifies. The saturation pressure, the saturation temperature and the depressurization rate are the critical parameters in determining the number of cells and the cell size distribution.

4.4.1. Batch foaming

In batch foaming, a polymer in disc or powder form is subjected to supercritical CO₂ without mixing. Depending on processing conditions, dissolved CO₂ decreases the glass transition temperature or melting point so that the polymer may be converted to the molten state. Several research groups have reported batch foaming of various polymers including biodegradable materials [154–170], where foaming is mainly applicable to

tissue engineering, tissue regeneration and protein encapsulation. Good control over porosity was possible in the reported studies by manipulation of temperature and pressure. The cell number density increased and the cell size decreased with increasing pressure and decreasing temperature. A high degree of supersaturation of dissolved CO₂ at high pressure and low temperature are responsible for such results. The viscoelasticity (elongational viscosity) of the polymer also plays a considerable role in determining the cell size and structure; it resists the elongation of cells during cell growth and restricts cell growth to small size. Such behavior was observed in branched PET and in blends of PS with liquid crystalline polymers [159,162].

Classical homogeneous nucleation theory is generally used to calculate the nucleation rate in foaming with supercritical CO₂. The energy barrier for nucleation in the theory can be calculated as a function of the interfacial tension of the binary mixture and the magnitude of the pressure drop. The theory suggests that the energy barrier and the interfacial tension decrease as the pressure drop increases. Consequently, the nucleation rate increases and a large number of small cells is obtained. In fact, both the pressure drop rate and the magnitude of the pressure drop determine the cell density and cell size in microcellular foaming. The higher the pressure drop rate the greater is the nucleation rate due to the high supersaturation rate. This allows only a short time for existing cells to grow and, consequently, favors formation small cells. Classical nucleation theory fails to incorporate the effect of the pressure drop rate. Moreover, a noteworthy study on CO₂-assisted microcellular foaming of PLGA is reported by Sparacio and Beckman [157] in which a minimum in cell size with increasing pressure, was found instead of the leveling off according to theory. A plausible explanation is low resistance to cell growth due to a large decrease in the melting point of the polymer and very low interfacial tension at high pressure.

4.4.2. Continuous microcellular foaming

In batch foaming, formation of single-phase polymer/CO₂ solution is governed by diffusion of CO₂ into a stationary polymer matrix. The major disadvantage of the batch process is that relatively low diffusivity of gas results in long cycle times. This is overcome in continuous microcellular foaming by providing rapid mixing of polymer and CO₂. An extrusion technique, suitable for handling viscous materials, is generally used for mixing polymer

and gas. In an extruder, the single-phase solution formation time decreases as high shear mixing decreases the gas diffusion distance (the striation thickness) [171]. Significant research and development efforts have been made to develop a continuous mode of production of microcellular polymers by extrusion [172–181]. In order to shape the polymer foam injection molding has been used where the polymer is foamed inside the die. Because dissolved CO_2 reduces the polymer viscosity, low processing temperature, good melt flow ability, and short cycle time are the advantages of using supercritical CO_2 in foam injection molding [178].

In continuous foaming, the arrangement for the formation of single-phase solution using extrusion technique involves an extruder with a CO_2 injection system and a static mixer. The amount of CO_2 injected into the polymer is always far below the solubility of CO_2 , thus avoiding phase separation prior to nucleation. As the residence time of the polymer– CO_2 mixture in the extruder and mixer is very short, an estimate of the time required to form a single-phase solution is important prior to continuous processing. The time can be estimated from convective diffusion theory [171,174]. The estimate for a typical polymer viscosity of 200 Pa·s suggests that single-phase solution formation can be achieved at industrial processing rates [174]. Splitting and reorientation of flows in the static mixer and shear action in the extruder cause the breakup of big bubbles into smaller ones and hence, enhanced mass transfer that shortens the time for formation of a single-phase solution. Rapid

depressurization of the solution through a nozzle then causes supersaturation of CO_2 and, consequently, the production of microcellular foam.

Park et al. studied effect of pressure drop rate on nucleation in continuous foaming at a given pressure drop by using nozzles with different dimensions [173]. They found that the cell density increased with increasing pressure drop rate (Fig. 4). This suggests that nucleation is affected by the time period over which the thermodynamic instability is induced in the polymer, as might be expected by competition between microcell nucleation and growth of the cells [173].

Supercritical CO_2 as a foaming agent has found application in the food industry, in the continuous production of expanded starch-based food products. An experimental foaming study along with a theoretical model explaining the mechanisms of bubble growth and collapse has recently been reported [182–185]. Unlike the traditional steam extrusion food process, foaming can be carried out at low temperature and low shear in the presence of supercritical CO_2 . This allows use of heat sensitive ingredients such as whey proteins, flavors and colors.

Despite increased attention to continuous foaming applications, only a few simulation studies are available characterizing the flow field and pressure distribution in a die [180] and predicting the bubble size distribution in a mold [186,187]. In these studies, predicted bubble sizes, showed considerable deviations from experimental results, probably because of invalid assumptions of uniform nucleation, atmospheric pressure in the unfilled region of the mold, and convection of bubbles

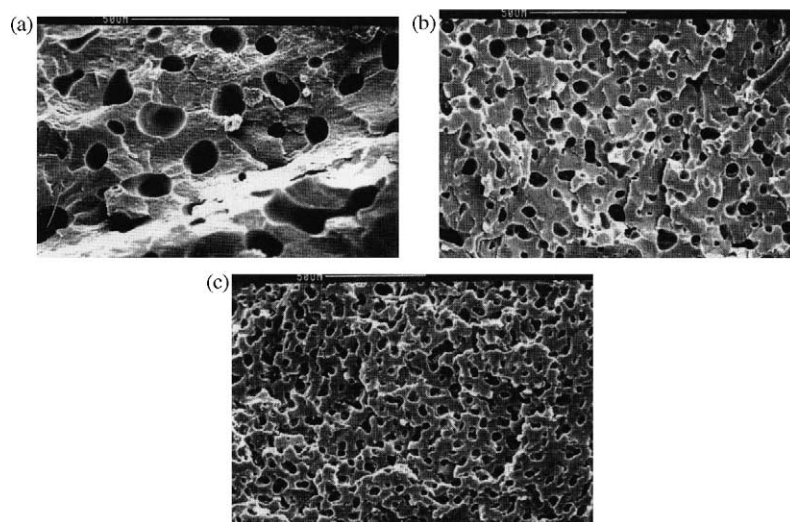


Fig. 4. SEM pictures of extruded HIPS for different pressure drop rates: (a) 0.076 GPa/s; (b) 0.42 GPa/s; (c) 3.5 GPa/s [173]. Reproduced from Park, Baldwin and Suh by permission of the Society of Plastics Engineers, USA.

during foaming [186,187]. In view of the growing interest in this technology, improvement in the simulations would be helpful to gain better theoretical understanding of the foaming process prior to commercial production.

4.5. Particle production

Better control of particle size, particle size distribution and morphology can be obtained by employing particle formation methods that use supercritical CO₂ as a solvent or antisolvent. With supercritical CO₂, different morphologies can easily be obtained by tuning process parameters such as the amount of dissolved CO₂, temperature, pressure, nozzle diameter and depressurization rate. Moreover, the additional challenges associated with traditional particle formation methods, such as solvent recovery and avoiding emissions of organic solvents, are absent. Milling, grinding and solvent crystallization/precipitation are the traditional particle formation methods commonly used in paint, toner and pharmaceutical industries. Milling and grinding are not suitable for a polymer having a low melting point or glass transition temperature mainly because of expensive cryogenic cooling required and heat dissipation occurred during processing. In pharmaceutical applications, where a drug is encapsulated in biodegradable polymer particles for controlled release, residual organic solvent is obviously undesirable. When supercritical methods do involve an organic solvent for particle production, better extraction of solvent is possible using supercritical CO₂ as an antisolvent because of low interfacial tension. These advantages have spurred adoption of supercritical CO₂ in particle formation technology despite the high pressures required.

For the past two decades, research on particle production using supercritical CO₂ has been rapidly growing. Existing methods that use supercritical CO₂ as a solvent or antisolvent have recently been broadly reviewed [188–190]. They include: rapid expansion of supercritical solutions (RESS), gas antisolvent crystallization (GAS), supercritical antisolvent precipitation (SAS), precipitation by compressed antisolvent (PCA), solution enhanced dispersion by supercritical fluid (SEDS), aerosol solvent extraction system (ASES), and particles from gas-saturated solutions (PGSS). To give a sense of these processes, they are compared in Table 3.

Much attention has been given to particle formation from biodegradable polymers used for pharmaceutical applications. With biodegradable polymers

Table 3

Comparison of supercritical processes for polymer particle formation

	RESS	GAS/SAS/ PCA	SEDS/ ASES	PGSS
Process	Semicon- tinuous	Semicon- tinuous	Continu- ous	Continu- ous
Gas quantity	High	Medium	Medium	Low
Organic solvent	Absent	Present	Present	Absent
Pressure	High	Medium	Medium	Medium
Separation of gas	Easy	Easy	Easy	Easy

supercritical CO₂ has been used frequently as an antisolvent. In antisolvent methods, a polymer solution in an organic solvent is expanded in supercritical CO₂ and extraction of the solvent by the CO₂ causes precipitation of the polymer as particles. The high diffusivity of CO₂ and its low surface tension are key factors in determining a wide range of applications [191]. Although CO₂ is not solubilized initially in the polymer in antisolvent methods, dissolution of CO₂ into the particles during extraction of the solvent affects the morphology. Depending on the plasticization of the polymer, foam, or hollow or dense particles are formed.

Among the methods listed above, only RESS and PGSS do not require an additional solvent other than CO₂. In RESS, the polymer is dissolved in supercritical CO₂ while in PGSS CO₂ is dissolved in the polymer. The RESS method is applicable to very few polymers due to the low solubility of most polymers in supercritical CO₂. The PGSS method for the production of polymer particles is a good choice as it utilizes the high solubility of supercritical CO₂ in most polymers. Compared with other available methods PGSS has big advantages for highly viscous, waxy, and low glass transition temperature polymers. Here, we mainly focus on PGSS, where the dissolution of CO₂ is mainly responsible for the production of particles. The PGSS method, which is still in its infancy, has recently been used to produce particles of powder polymer coatings and biodegradable polymers [192–201].

In PGSS, a molten polymer is saturated with gas at high pressure and the gas-saturated solution is expanded through a nozzle from a supercritical to sub-critical pressure. The gas-saturated solution has low viscosity due to an increase in free volume, as explained above. During depressurization, supersaturation of the gas leads to a rapid expansion of the polymer melt and gas so that fine particles are formed. The particles are solidified by the cooling effect of the expanded gas. Moreover, the gas is also easily

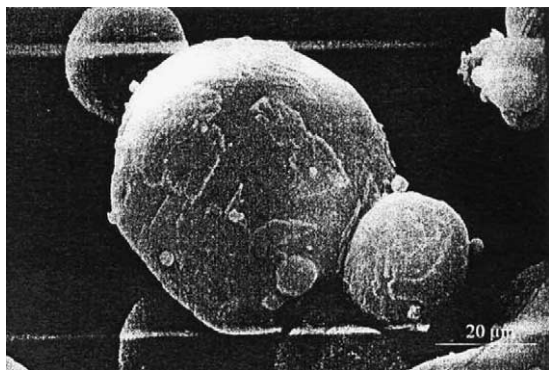


Fig. 5. Particles of polyester produced at 321 K in the PGSS process [196]. Reproduced from Weidner, Petermann, Blatter and Rekowski by permission of Wiley–VCH Verlag GmbH, Weinheim, Germany.

separated and can be recycled. The method has been patented by Mandel et al. [192,194] and Weidner et al. [193]. It can be applied in batch mode, where a single-phase solution is formed using a mechanical stirrer, and, in continuous mode, where a static mixer is used to saturate molten polymer with a gas.

Recently, micron size particles of acrylic coatings, polyester–epoxy systems and low-melting polyester coatings (Fig. 5) were produced by a continuous PGSS process [196]. Particles with different morphologies, foam and dense, were obtained by tuning the processing conditions that determine the amount of CO_2 dissolved. Nowadays, special attention is being given to biodegradable polymers, as the product quality of pharmaceuticals can be significantly improved, using PGSS, by controlling their physical properties, such as particle size, particle size distribution and morphology. Micron-size particles from supercritical CO_2 -plasticized PEG, PEO, and poly(DL-lactic acid) ($\text{P}_{\text{DL}}\text{LA}$) melts of various molecular weights were produced by this method [195,197–201]. It was even possible to produce particles below the melting temperature of the polymer, which is always an important concern in processing polymers with heat-sensitive drugs. Weidner et al. [198] and Kilzer and Petermann [201] studied the effect of the mass flow-rate ratio of CO_2 (in excess to its solubility) to polymer on the production of particles. They found that the particle size decreased with increasing ratio and that the effect was less pronounced at high ratios. In PGSS it is possible to obtain different morphologies and particle sizes by tuning processing conditions. These properties mainly control the degradation rate of biodegradable polymer particles and hence, the release rate of an encapsulated drug. In the reported studies, the particle size was reduced with increasing pressure as well as with decreasing

temperature. Moreover, a narrower particle size distribution was obtained when the pressure was increased and the temperature was decreased. All these favorable results are directly related to the high solubility of CO_2 at high pressures and low temperatures.

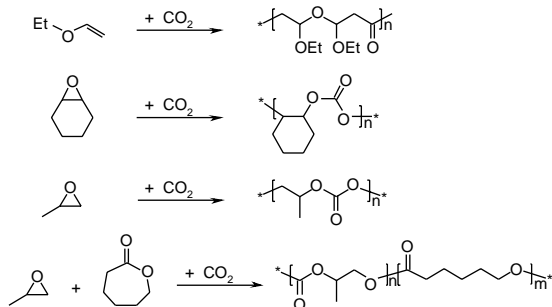
Thus, the use of supercritical CO_2 in particle production is very convenient from several points of view. Encapsulation of drugs in biodegradable materials in general is an active field of investigation in which new developments are continually reported [201–205]. Recently, CO_2 was used as a carrier for impregnating a polymer (disc or particles) with a drug from solution; CO_2 plasticizes the polymer, the allowing the diffusion rate of the drug to be controlled. However, it must be stressed that the supercritical methods are still compound-specific and at the moment no universal method is available.

4.6. Polymerization in supercritical CO_2

Cooper [1] and Kendall et al. [5] have reviewed synthesis of polymers in supercritical CO_2 . Since, the most recent work, dated 1999–2000, little fundamental progress has been reported. However, some refinements of earlier methods and investigations of new polymerizations are discussed.

Step-growth polymerizations under supercritical CO_2 have been widely studied for the production of polycarbonates, polyesters and polyamides [206–212]. In these polymerizations, attention is mainly paid to the late stage of the process, where the main advantage in using CO_2 is the reduced viscosity of polymer as compared to the usual melt synthesis. In supercritical CO_2 -assisted polymerizations the reduction in viscosity decreases the mass transfer resistance, which is always high in polymerization reactions due to the viscosity of the polymer, and consequently, the conversion is increased. As the reduction in viscosity depends on the amount of CO_2 dissolved, the solubility of CO_2 in the synthesized polymer plays a crucial role in determining the ultimate molecular weight and properties of the polymer.

Very recently, academic laboratories have shown interest in polymerizations where CO_2 acts a comonomer as well as a solvent [213–216]. An overview of these polymerizations is given in Scheme 2. In all cases, the final yield and polymer molecular weight are strongly dependent on temperature, pressure, reaction time, chemical composition, solubility of the catalyst in supercritical CO_2 , and solubility of CO_2 in the polymer. In cationic copolymerization with ethyl-vinyl ether



Scheme 2. Overview of CO₂ copolymerization reactions [213–216].

[216], the amount of copolymerized CO₂ increases dramatically in the transition from subcritical to supercritical conditions. This is due to the extra stabilization of the carbocation (an intermediate species in the propagation of the kinetic chain) by supercritical CO₂. Moreover, at higher conversions when a substantial quantity of polymer is present, the solubility of CO₂ and polymer swelling become crucial factors controlling the ultimate polymer properties.

All the recent literature clearly indicates a shift of attention toward the later stages of the polymerization process and toward the ultimate properties of the polymer. Accordingly much current effort is directed toward establishing, at least on an empirical level, relations between processing parameters (composition, temperature, pressure, CO₂ solubility, surfactant type and amount etc.) and the final polymer properties.

5. Conclusions and outlook for the future

Because of its high solubility in many polymers, supercritical CO₂ is a valuable tool in polymer processing. Moreover, the replacement of conventional organic solvents with an environmentally less harmful fluid, CO₂, is a major motivation for its use. FT-IR spectroscopy, which is a very good tool to determine the interaction of CO₂ with a polymer at the molecular level, may be used to obtain a rough estimate of CO₂ solubility from the width of the CO₂ bending-mode spectra at low temperature. On the quantitative level, a compendium of experimental phase equilibrium data and the modeling of those data with different theories for various molten polymers and supercritical CO₂ at high temperatures and pressures are needed to utilize the potential of supercritical CO₂ in polymer processing. Thus, there is motivation to generate data under real processing conditions rather than to rely on off-line measurements. In thermodynamic modeling, a particular EOS (S–L, P–V, M–B, P–R, SAFT, or the EOS of

Kumar et al.) cannot be endorsed generally at this stage for prediction of CO₂ solubility because the predictive capabilities of most EOSs have not yet been tested for the polymer systems data available in the literature. However, the deviation between the predicted and the actual critical temperature and pressure values for CO₂ can be considered in selecting a particular EOS. The lattice theory based EOSs are used more frequently than off-lattice methods because of their simpler approach. However, the cubic EOS (P–R EOS) with appropriate mixing rules in order to increase the accuracy may also be useful for modeling thermodynamic properties at high temperatures and pressures. Recently, the temperature dependence of CO₂ transport in amorphous PE melt has been studied using molecular dynamics simulation [217], but only at low pressures. Simulation, an inexpensive technique for studying the penetrant diffusion and solubility at high pressures, may sometimes be a good substitute for experimental work.

In CO₂-assisted polymer processes, knowledge of the reduction in polymer viscosity in the presence of dissolved CO₂ is essential as it allows processing at low temperatures. Substantial reductions in viscosity have been reported for polymer melts in the presence of dissolved CO₂. Despite a large number of applications, experimental rheological studies are still lacking for various industrially useful polymer melts in which the solubility of CO₂ is high. In the absence of experimental viscosity data, free-volume theories may deserve some reliance as they are based completely on the physical properties of the pure components.

Various applications of supercritical CO₂ have been reported: polymer modification, polymer composites, polymer blending, microcellular foaming, particle production, and polymerization, where CO₂ plays the role of plasticizer or solvent or antisolvent. Relatively little attention has been given to the PGSS method of polymer particle formation, which utilizes the solubility of CO₂. It could be a good choice among the various particle production methods. It must be tested for specific polymers as no extra solvent is used. Future developments in the area of CO₂-assisted polymer processing are very difficult to predict, mainly because of continuing rapid developments and applications in a variety of processes. Very recently, new uses of supercritical CO₂ have been reported for: increasing ionic conductivity of PEG-salt complexes [218,219], modifying topographic features of polymer films and tuning their adhesion on various substrates [220], dispersing low molecular weight chemicals into pre-formed polymeric products [221], selectively and quantitatively cross linking biodegradable polymers

[222], assisting reactive extrusion [223], drawing of high molecular weight PE [224] and PET [225] fibers, enhancing water absorbing properties of hydrophilic polymers [226], assisting electrospinning processes for production of polymer fibers [227], and producing polymer templates [228–231].

The wide range of applications clearly suggests a bright future for CO₂ assisted polymer processing, but it also indicates the need for deeper understanding of specific interactions in polymer–CO₂ systems, for the accumulation and modeling of a variety of experimental rheology and phase equilibrium data, and for the simulation studies to supplement experimental work.

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