

Supercritical Fluid Deposition of Metals on Polymer and Composite Materials

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Abstract

Metal/ polymer and metal /composite materials are currently the focus of much research activity in various fields of nanotechnology. The deposition of metal films and nanoparticles on polymeric surfaces can exhibit unique properties of conductivity, reflectance and surface plasmon resonance useful in SERS (surface enhanced Raman spectroscopy).

Novel applications exploiting the unique properties of polymeric materials impregnated with metal nanoparticles and metal films are found in various research areas including applications in fuel cells, electrodes, catalyst, and biological and chemical sensors.

Introduction

Supercritical carbon dioxide has the ability to plasticize polymers and this feature is important in the impregnation of these polymers with metallic nanoparticles and metallic films. In addition, supercritical CO₂ has no surface tension and therefore is able to penetrate high aspect ratio nanopores and trenches to deposit metals. This paper discusses the supercritical fluid deposition technique as an alternative to chemical vapor deposition and atomic layer deposition techniques. Examples are presented demonstrating the supercritical fluid technique including the deposition of metals into a variety of polymeric materials.

Supercritical Fluid Deposition of Metals on Polymer and Composite Materials

Comparison of CO₂ Properties with Other Solvents

Solvent	Viscosity (cP)	Surface Tension (dynes/cm)	Density (kg/m ³)
Liquid CO ₂	0.08	1.5	870
Supercritical CO ₂	0.03 (35C, 75 atm)	0	300 (35C, 75 atm)
Methanol	0.54	22.1	800
1,1,1-Trichloroethane	0.81	25.2	1300
Water	1.0	72.0	1000
Isopropyl Alcohol	2.4	21.8	785

Polymer Swelling in CO₂

CO₂ sorption into polymer lowers T_g

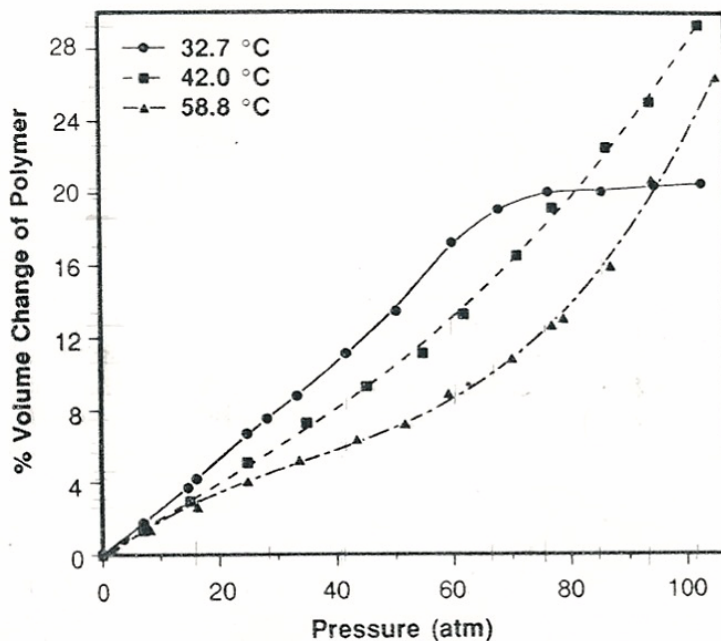
Swelling is increased if T_g is exceeded

Swelling decreases polymer/polymer interactions and therefore reduce the δ

Additional polymer/polymer interactions can be reduced by a cosolvent

Pressure pulsing cracks polymer before polymer/polymer interactions are reestablished.

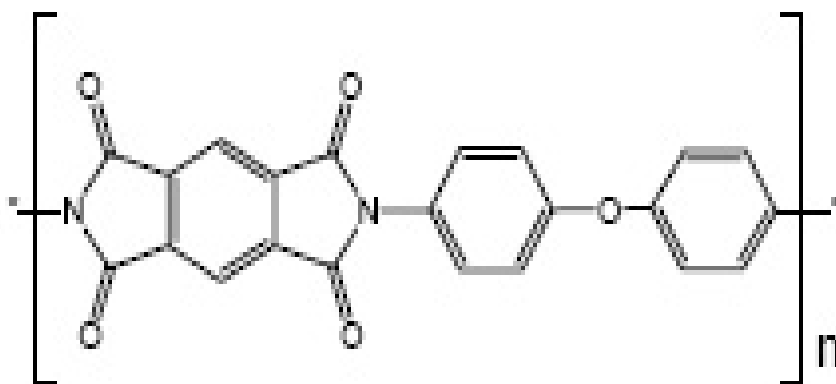
SWELLING AND SORPTION IN POLYMER-CO₂



Organometallics

- Many organometallics are soluble in supercritical CO₂
 - Pt
 - Pd
 - Cu
 - Au
 - Ni
 - Rh
- Examples:**
Pt(II) (ACAC)₂
[Ag (COD)HFA]₂

Chemical Structure Polyimide Film



Procedure

- Add polyimide film and organometallic to vessel (no contact)
- Pressurize with CO₂ (196 bar)
- Heat 313 to 473 K
- Static , Batch reaction (3- 24 hrs)

Deposition of Metals into Composite Material

- Nano structured materials
- Catalysts
- Sensors
- Optics
- Electronics
- Properties depend on size of particles

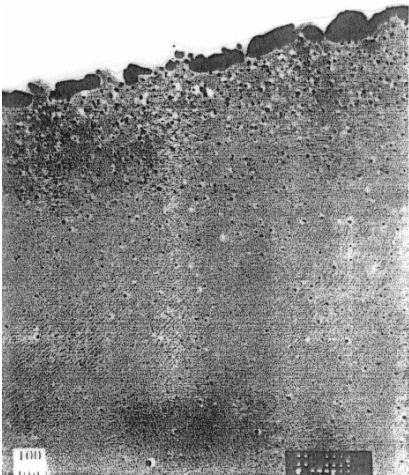
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Equipment & Infusion Conditions

Supercritical Fluid Extractor	Applied Separations' <i>Spe-ed</i> SFE-2
Extraction Cell:	3mL
Pressure:	5000 psi
Temperature:	110°C
Time:	30 - 180 minutes



TEM of the Air-Side of the Poly(amide) Acid Film at 37,500 Magnification



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Conclusion

The supercritical fluid deposition of metals into polymers and composite materials is a viable alternative to the standard chemical vapor deposition and atomic layer deposition techniques.

Fully cured polyimides and partially cured polyamides can be infused with an additive to produce a silvered surface.

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