INTRODUCTION

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NANOCOMPOSITES OF HIGH PREFORMANCE THERMOPLASTIC POLYMERS USING EPOXY AS PROCESSING AID

A Thesis Presentation by

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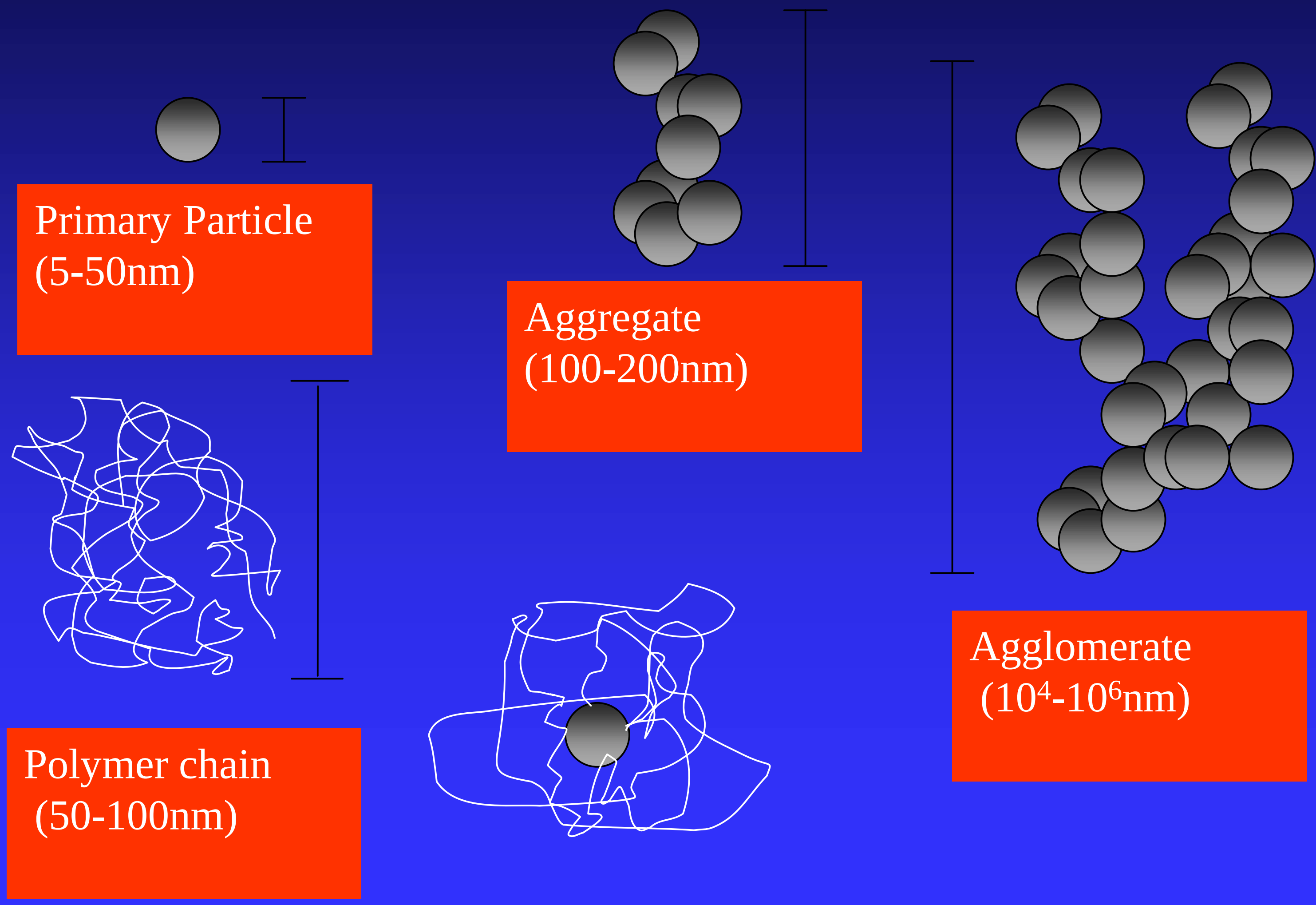
ISSUES WITH HIGH PERFORMANCE POLYMERS

- Processing temperatures are high ~ 300ºC
- Nanoparticles, if compounded, may provide barrier against solvents and higher heat distortion temperatures
- Melt-mixing of nanoparticles difficult due to high temperatures and high viscosity
- Non-reactive solvents are not welcome due to extra steps in solvent removal.

WHY NANOCOMPOSITES ?



ISSUES WITH NANOFILLERS

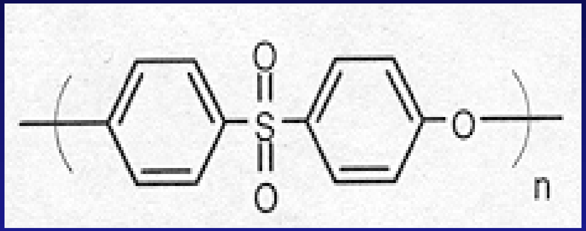
- Polymer-filler compatibility
- Aggregate formation
- Degradation due to shear heating

TYPICAL APPLICATIONS

Application area	PES (350°C) (Ultrason)	PBT (250°C) (Ultadur)	PPO (280°C) (Noryl)	PEI (350°C) (Ultem)	PEEK (390°C) (Victrex)
Automotive	■	■	■	■	■
Consumer		■	■	■	
Electrical /electronics	■	■	■	■	■
Industrial Building &construction	■	■	■		■
Medical	■	■		■	
Packaging		■	■	■	
Hot water fittings	■		■		
Coatings					■

MATERIALS USED

PES



Ultason 1010 natural, supplied by BASF

- Glass transition temperature: 218 °C
- Specific Gravity: 1.2-1.6
- Typical processing temperature: 350 °C
- Decomposition temperature: 400°C

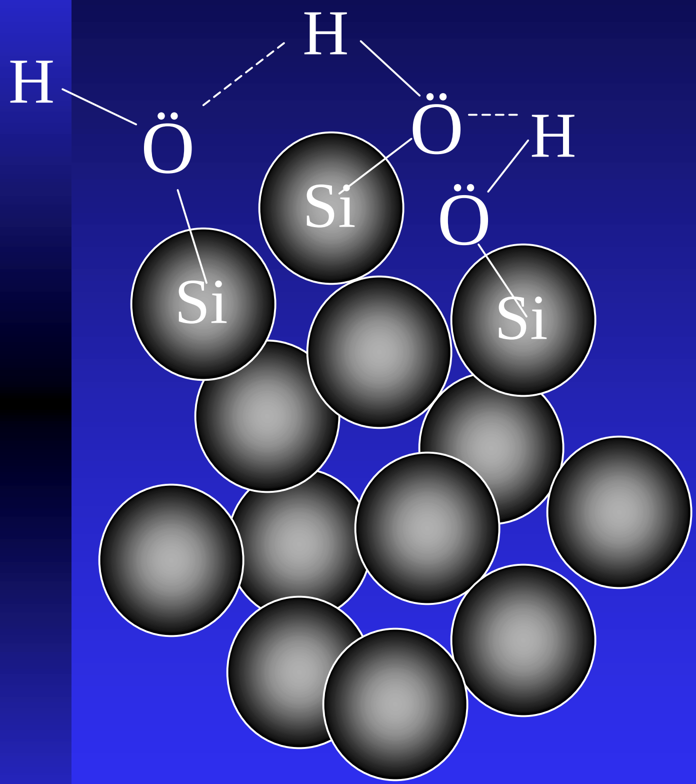
NANOPARTICLES

- Fumed Silica (Aerosil 90 and 200) Degussa Corps.

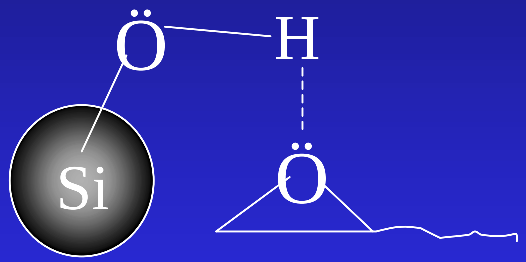
Property	Aerosil 200	Aerosil 90
Avg. primary particle size(nm)	12	20
Specific gravity(approx.)	2.2	2.2
Bulk density (g/CC)(approx.)	0.030	0.080
Silanol groups per sq.nm	2-3	2-3

SILANOL GROUPS PROVIDE CHANCES OF INTERACTION WITH EPOXY

HYDROGEN BONDING IN FUMED SILICA



Agglomerates of fumed silica



Hydrogen bonding between Si-OH and epoxy groups improve dispersion

EPOXY AS REACTIVE SOLVENT

Thermoplastic polymer systems	Literature	Observation
Polyphenylene ether (PPE)	Meijer et al.	▪ reduced processing temperature ▪ better adhesion with glass and treated carbon fibers
Polyethersulfone (PES)	Cracknell et al. Inoue et al.	▪ epoxy toughening by PES ▪ regimes of phase separation
Polysulfone (PSU)	Park et al.	▪ epoxy toughening ▪ reaction-induced phase separation
Polyetherimide (PEI)	Bucknell et al. Meijer et al. Pascualt et al.	▪ epoxy toughening ▪ thermodynamics of phase separation

ROLE OF EPOXY AS PROCESSING AID

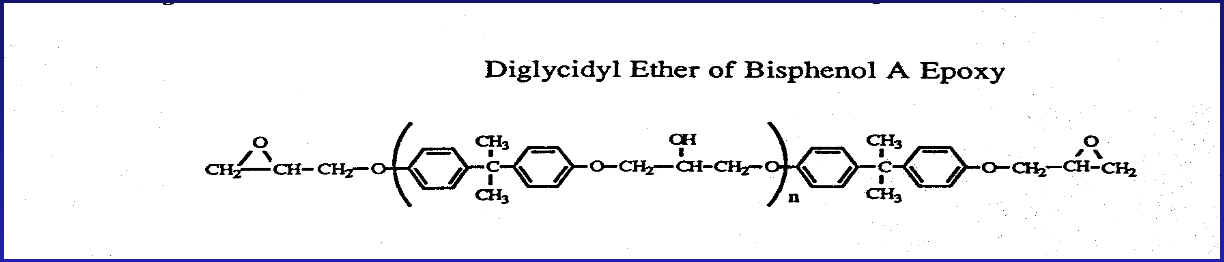
- Epoxy lowers the processing temperatures
- Epoxy phase separates after curing to form the dispersed phase
- Mechanical properties are improved/restored upon epoxy curing
- Epoxy, when cured, potentially forms coating around silica particles.

OBJECTIVES

- Exploit the use of epoxy to lower the processing temperatures of PES.
- Use PES-epoxy system as a model to establish that epoxy can be used as dispersant of nanoparticles in high performance thermoplastic polymers.

EPOXY SYSTEM

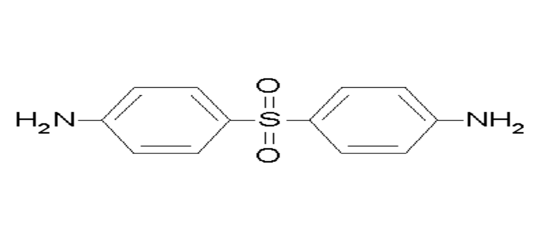
- **Epoxy resin** (DGEBA Epon 828) Shell Chemical Company



T_g: -18°C and sp.gravity: 1.17.

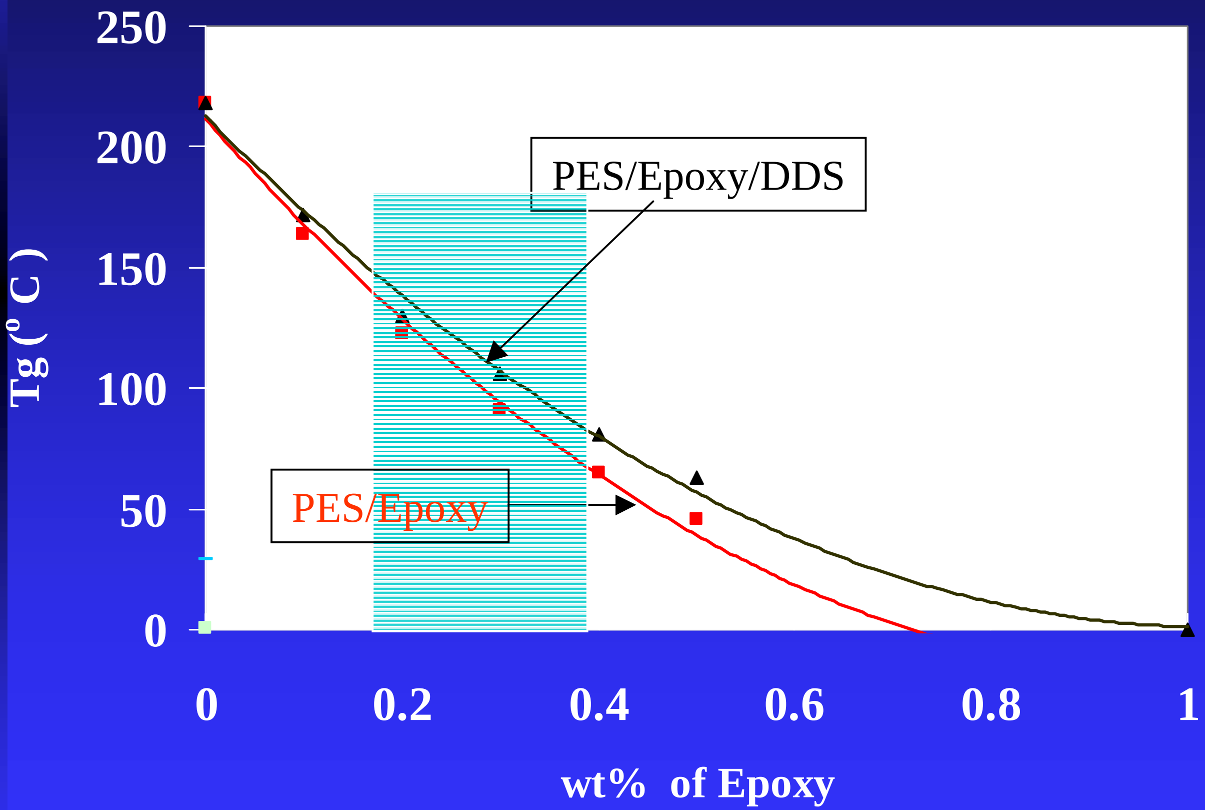
- **Hardener:** Diaminodiphenyl sulfone (DDS)- HT 976; Ciba Specialty Chemicals

Cure Temp,°C	Cure Time(min)
180	30
200	8
225	5



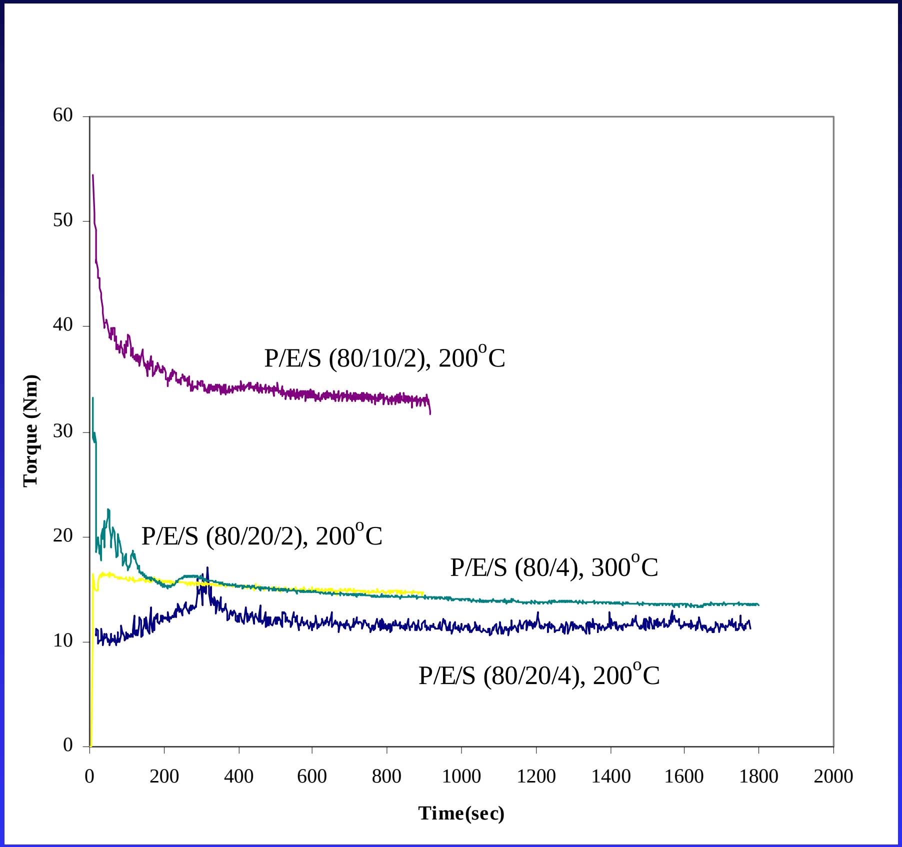
REDUCTION IN GLASS TRANSITION

Emphasis: 10-30 wt% epoxy



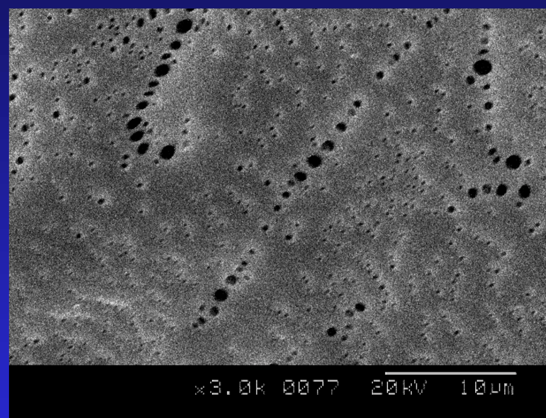
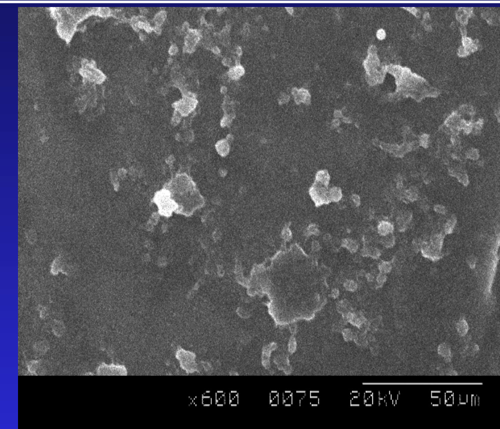
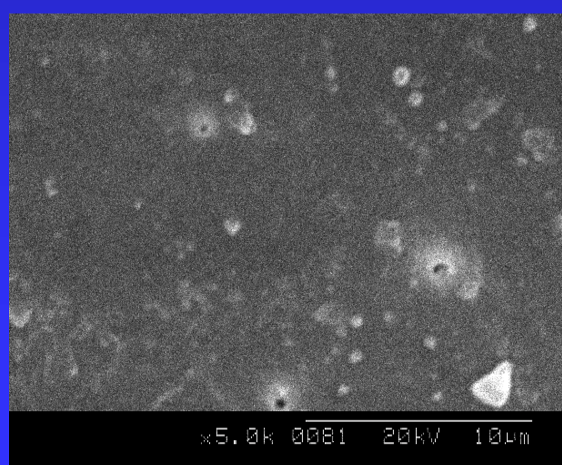
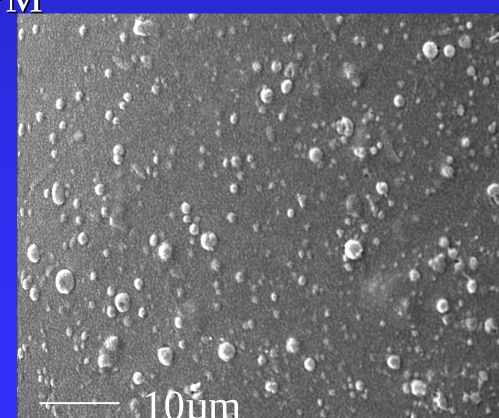
Composition of interests in this study

PROCESSABILITY IN PRESENCE OF EPOXY



Mixing torque vs. time illustrating the use of epoxy as processing aid.

EFFECTS OF MIXING TEMPERATURE AND SPEED OF MIXING

PES/Fumed Silica / (100/2)Mixed at 280°C	PES/fumed silica (100/2)Mixed at 300°C
50 RPM 	50 RPM 
100 RPM 	100 RPM 

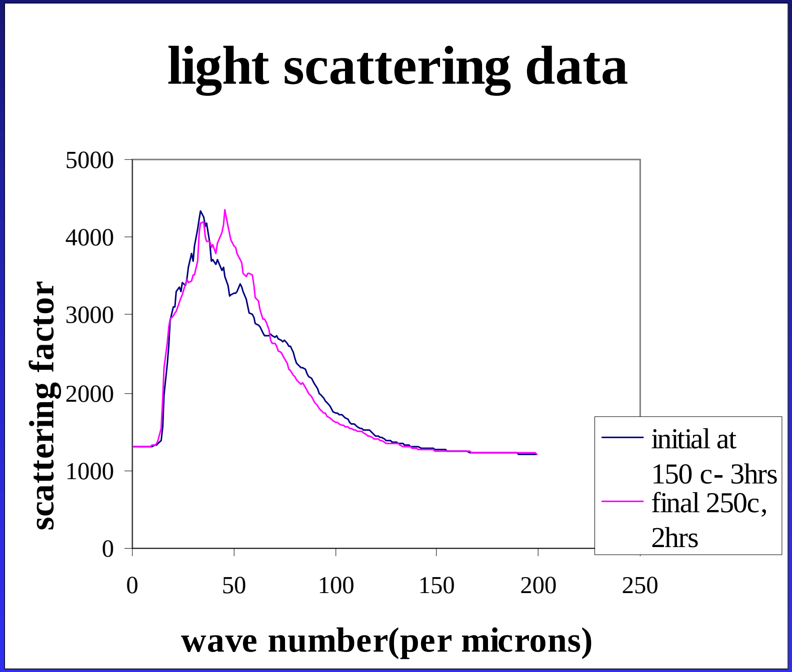
SAMPLE PREPARATION

- Samples prepared by melt-blending
- Epoxy and fumed silica premixed at 80-90°C for 30 min.
- Premixed fumed silica-epoxy melt-blended with PES in Brabender Plasticorder at

  $T=T_g + 50C$.
- Mixing time: 30 min.
- RPM: 50-100
- Hardener mixed for the last 5min.

TEMPERATURES FOR EPOXYCURING

- Two-stage curing confirmed by light-scattering data.
- Number of smaller sized domains increases in two-stage curing.



EVALUATION OF DISPERSED MATERIALS

- Dispersion of fumed silica analyzed by SEM and TEM
- Barrier to diffusion of dichloromethane and methanol tested at room temperature
- Tensile and fracture strengths
- Heat distortion temperature

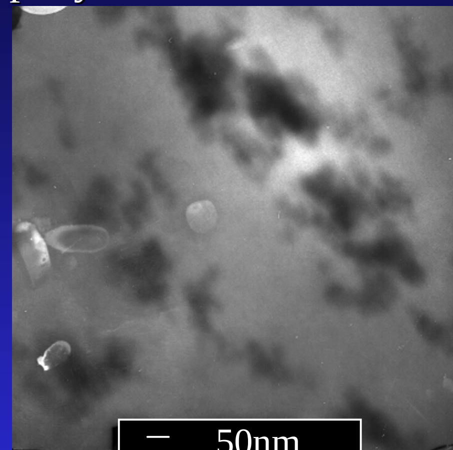
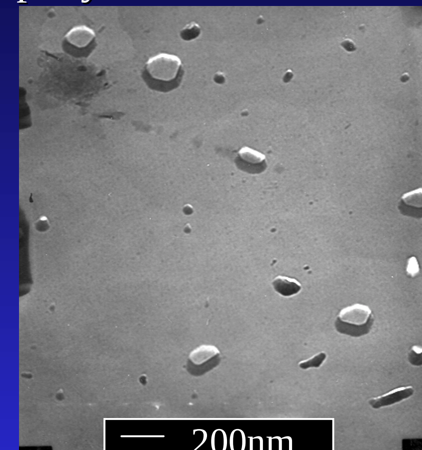
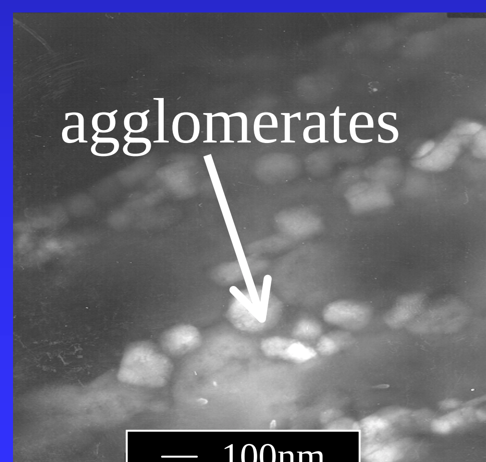
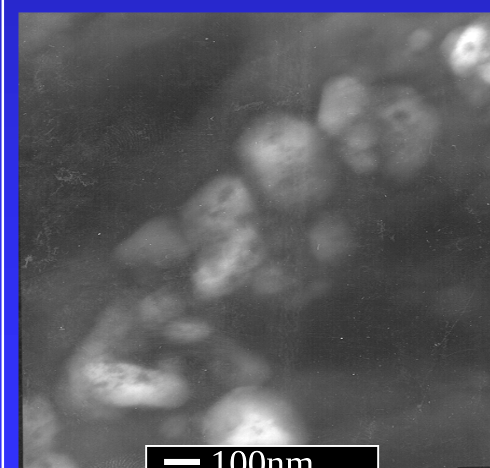
SEM AND TEM

TEM	SEM
Scales of individual particles	Scales of microns
Area under observation is small	Provides good picture of dispersion over large area
Staining confirmed epoxy coating	No staining needed
Distribution of size of particles cannot be characterized	Image analysis provides scale of particle segregation

SAMPLE PREPARATION FOR TEM

- Fumed silica particles can be observed without staining of samples
- Samples of 50-100 nm thickness prepared by ultra-michrotome
- Samples stained with RuO_4 for about 2-3 minutes for investigation of epoxy coating of silica particles

MUCH IMPROVED DISPERSION DUE TO EPOXY

<table>
<tr>
<td>PES/Fumed Silica=80/2
CURED EPOXY
Unstained</td>
<td>Epoxy: 10 wt%
</td>
<td>Epoxy: 20 wt%
</td>
</tr>
<tr>
<td>PES/fumed silica=100/4
NO EPOXY
Unstained</td>
<td></td>
<td></td>
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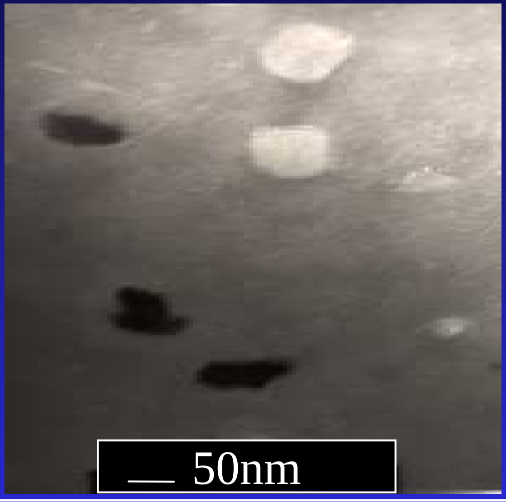
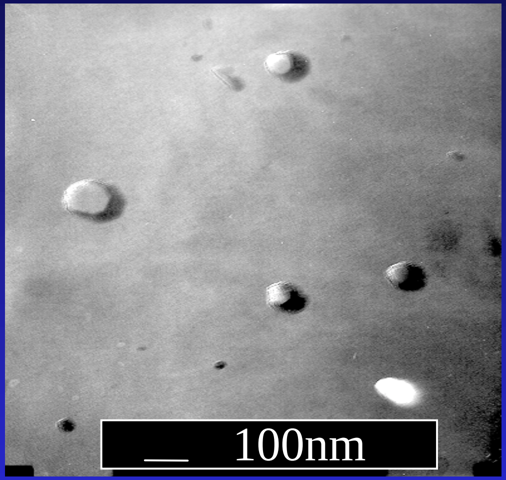
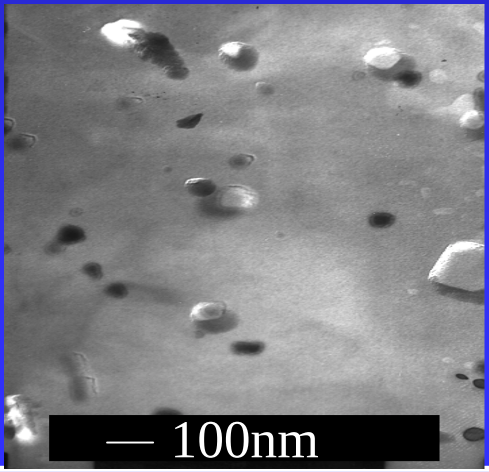
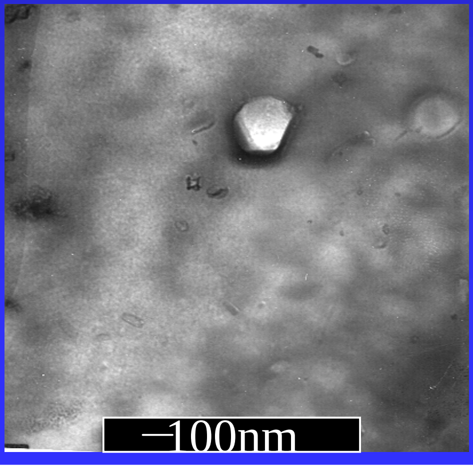
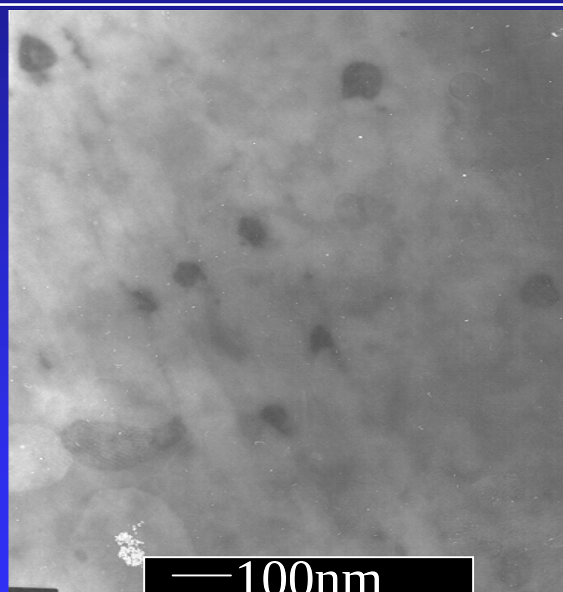
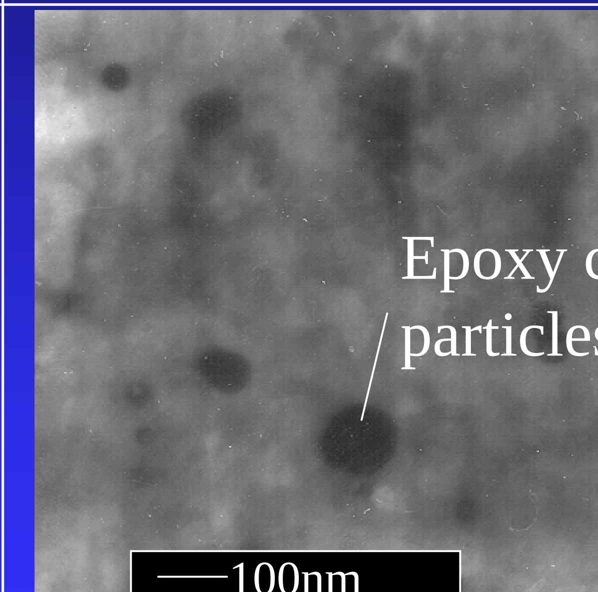
EPOXY CURING HAS NO EFFECT ON SIZE OF SILICA PARTICLES

PES:Epoxy = 80:20 Uncured epoxy	Fumed silica: 10 wt% 	Fumed silica: 4 wt% 
PES:Epoxy =80:20 Cured epoxy	Fumed silica: 10 wt% 	Fumed silica: 4 wt% 

STAINING REVEALED EPOXY-COATED SILICA PARTICLES

PES/Epoxy=80/20 Uncured epoxy Fumed silica: 2 wt%	PES/Epoxy=80/20 Cured epoxy Fumed silica: 2 wt%
	

CURING HAS NO EFFECT ON PARTICLE SIZE

SUMMARY I

- No agglomerates in presence of epoxy
- Typical dispersed particle size ~30-100 nm
- Epoxy coating around fumed silica particles apparent in stained samples
- Dispersed particles do not agglomerate due to curing of epoxy
- Spatial homogeneity of dispersion must be checked by SEM

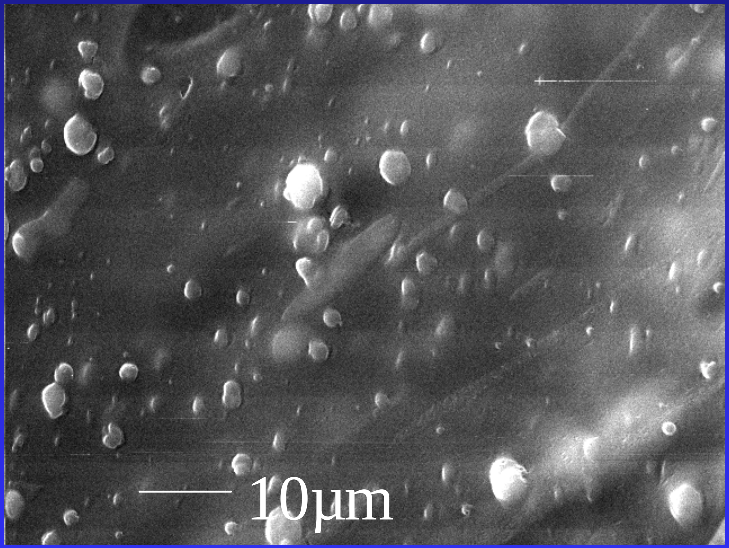
ANALYSIS BY SEM

- Cured samples cold fractured in liquid N_2
- Fractured surface etched in dichloromethane
- Some cured epoxy particles are lost during etching, leaving holes in the PES matrix.

SCALE OF SEGREGATION USING SEM

- PES/Epoxy /DDS (80/20/1:1)

Cured at 200°C , 1hr

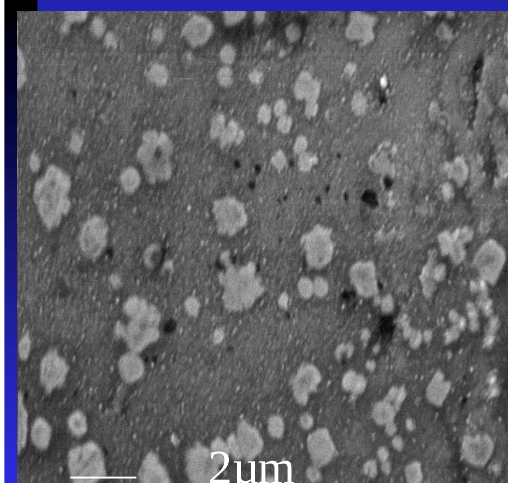


SEM SHOWS GOOD QUALITY OF DISPERSION

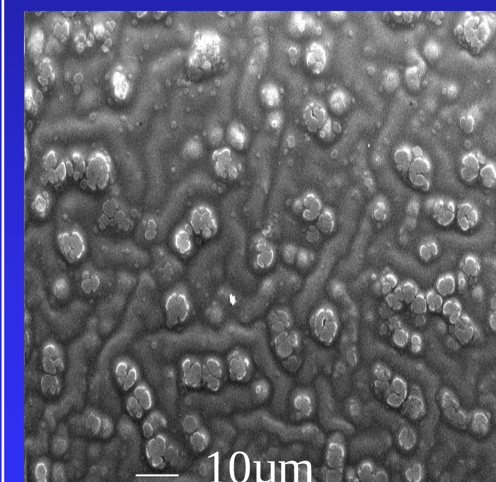
DISPERSED PARTICLES DO NOT AGGLOMERATE DUE TO STAGED CURING

- PES/Epoxy/Fumed Silica /DDS (80/20/2/1:1)

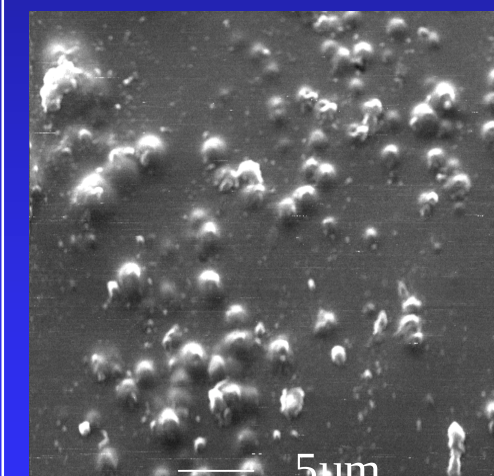
Cured at 200°C , 1hr



Cured at 200°C, 2hr



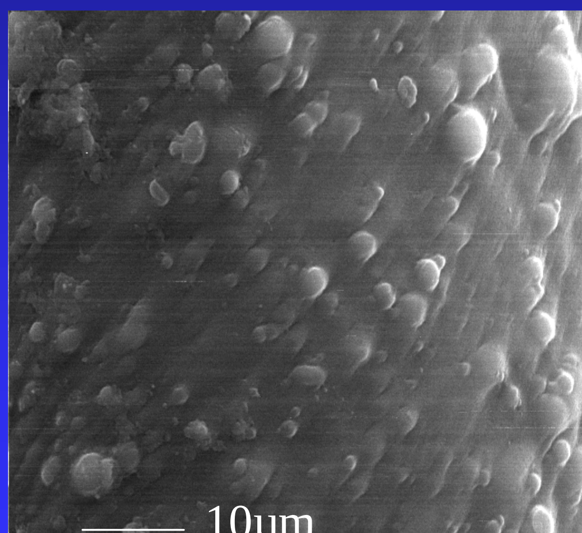
Postcured at 250°C, 1hr



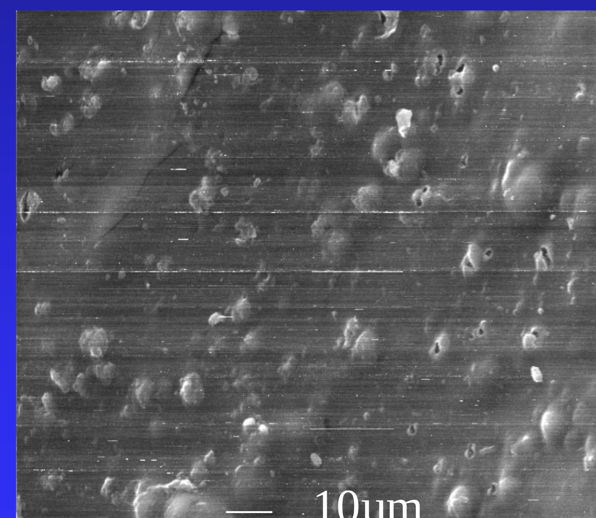
DISPERSED PARTICLES DO NOT AGGLOMERATE DUE TO STAGED CURING

- PES/Epoxy/Fumed Silica /DDS (80/20/2/1:1)

Cured at 200°C, 5.5hr

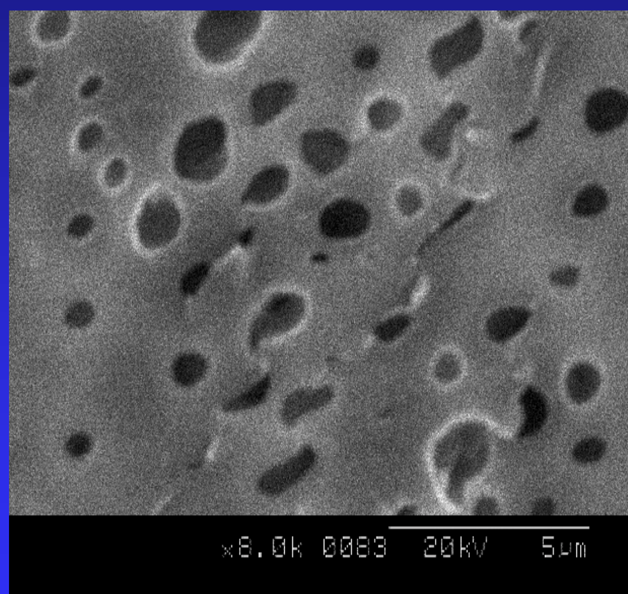


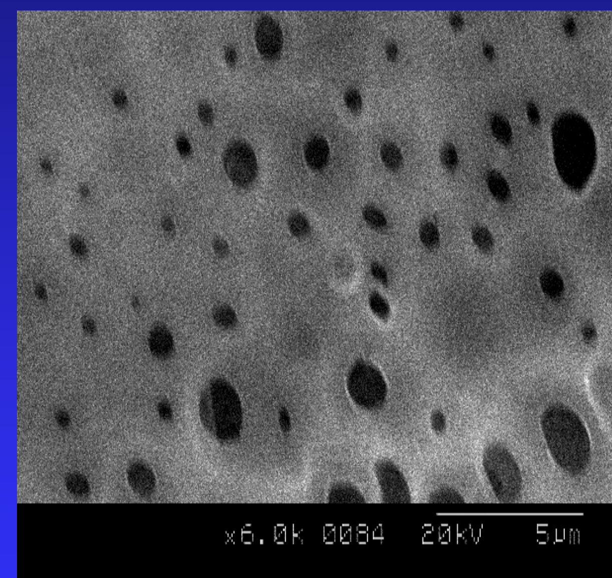
post cure at 250C , 2.5 hr



CHARACTERIZATION USING SEM

PES/Epoxy/Silica /DDS (80/20/10/1:1)	PES/Epoxy/Silica /DDS (80/20/4/1:1)
Cured at 200°C , 2hr	Cured at 200°C, 2hr





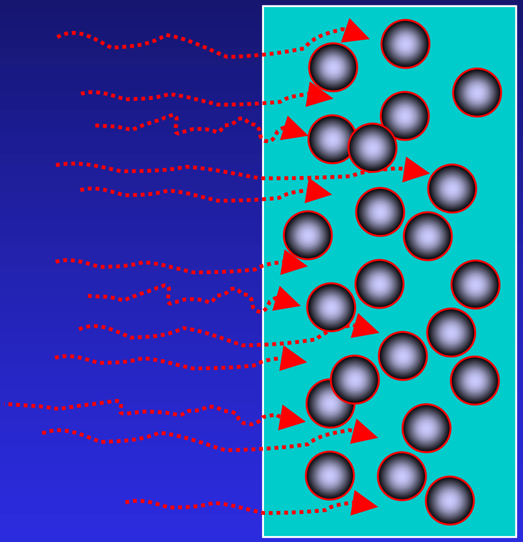
Scale of segregation by image analysis

Sample	Comp -osition	Cure conditions	Characteristic scale of segregation (µm)
PES/epoxy/ fumed silica	80/20/2/1	200ºC, for 1 hour	1.355 and 2.631
	80/20/2/1	200ºC, for 2 hours	2.9457 and 5.8915
	80/20/2/1	200ºC, for 5.5 hours	0.8395 and 1.6791
	80/20/2/1	200ºC, for 2 hours and postcured at 250ºC, for 1 hour	1.1616 and 2.3233
	80/20/4/1	200ºC, for 2 hours	1.1845 and 2.3691
	80/20/10/1	200ºC, for 2 hours	1.4924 and 2.9849
PES/fumed silica	95/5	Mixed at 280ºC, 100 rpm	1.7979 and 3.5959
	95/5	Mixed at 300ºC, 50 rpm	5.6359 and 11.2719

SUMMARY II

- Mixing and dispersion is good in the presence of epoxy
- Dispersion to almost individual fumed silica particles now achievable
- Coating of epoxy around silica particles apparent from TEM of stained samples

BARRIER TO SOLVENT DIFFUSION

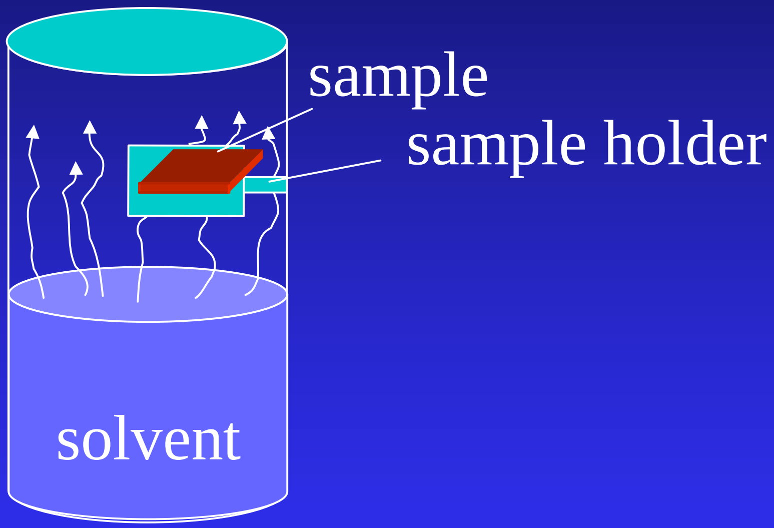


- Solvent molecules follow tortuous paths
- Better if particles are platelet types

BARRIER PROPERTIES OF PES-EPOXY-SILICA SYSTEMS

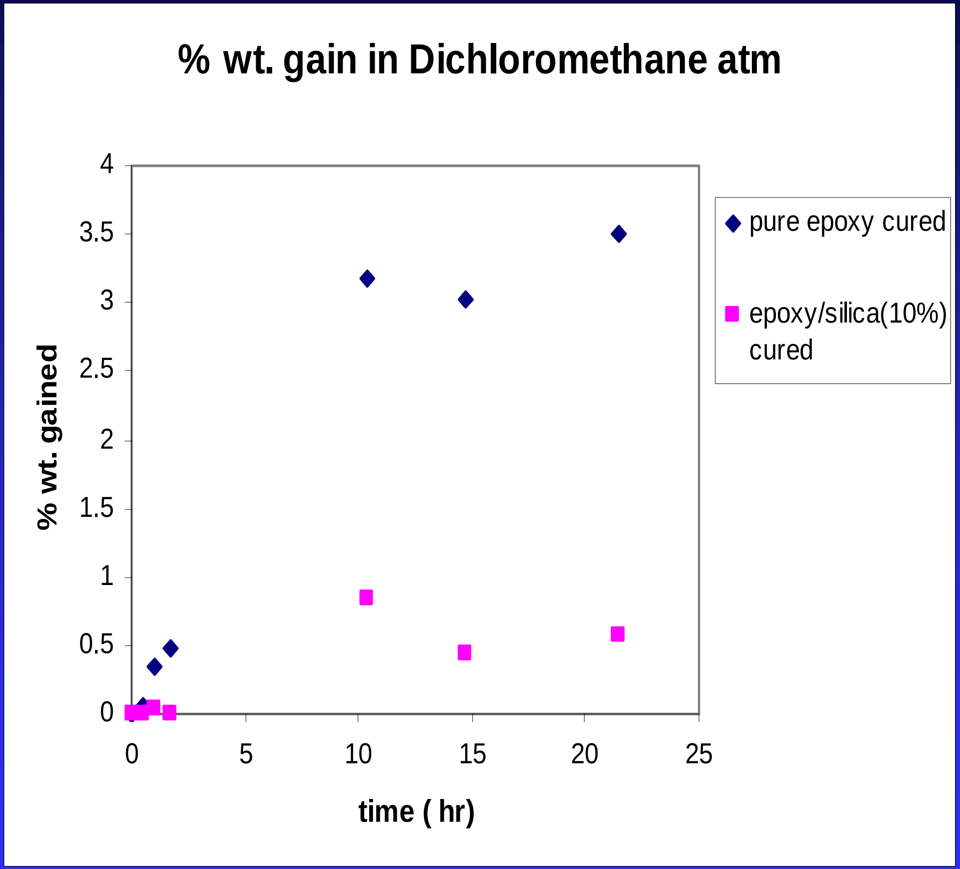
- Sample specimen: Circular disk with 50mm diameter and 3.175mm thickness (ASTM D543)
- Specimen hanged in closed chamber in saturated solvent atmosphere at room T
- Specimen weighed after regular intervals of time

MEASURING BARRIER PROPERTIES



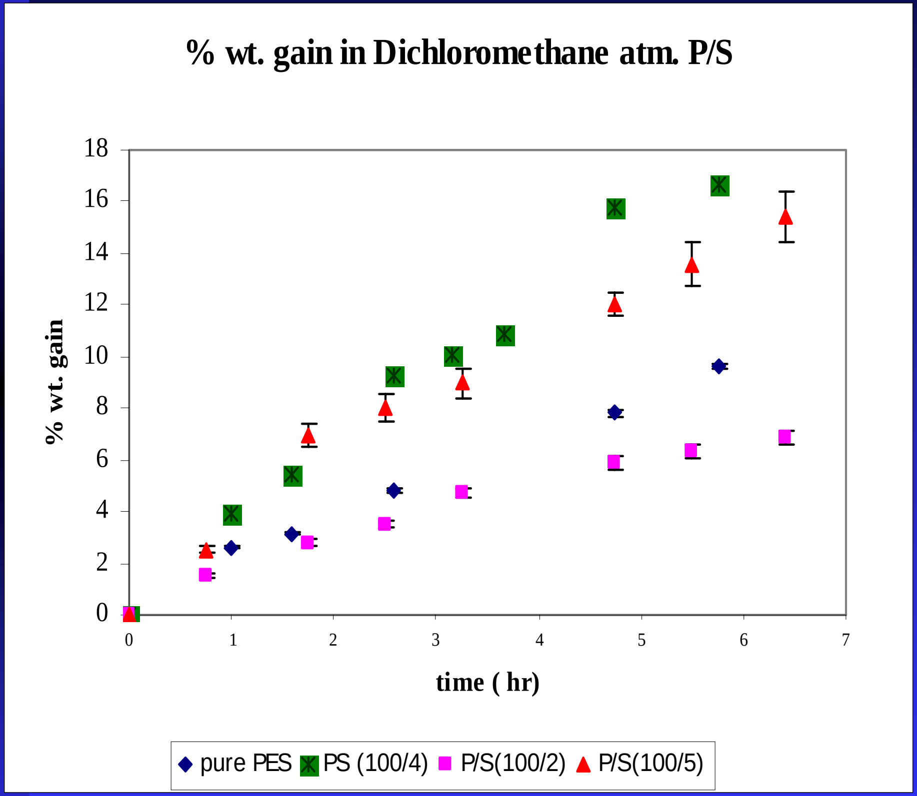
Solvent uptake/weight of non-silica (i.e., polymeric) part

EPOXY-SILICA SYSTEM



Fumed silica reduced solvent uptake per unit weight of cured epoxy

PES-fumed silica system



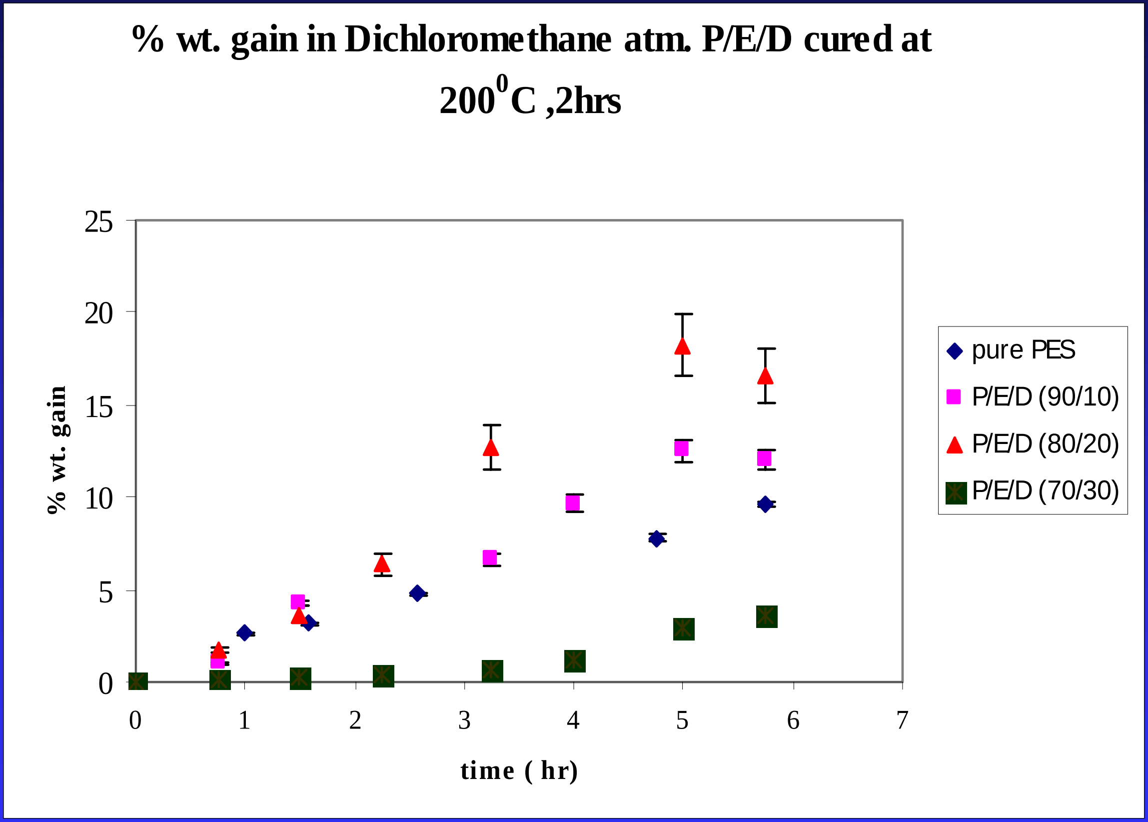
- 2 wt% fumed silica reduced uptake over PES
- 4 and 5 wt% silica increased uptake over PES
- Methylene chloride being non-polar does not get absorbed by fumed silica

AGGLOMERATES FORMED WITH 4 AND 5% FUMED SILICA DID NOT PROVIDE BARRIER TO SOLVENT DIFFUSION

INCOMPLETELY CURED EPOXY INCREASES ABSORPTION

System:
PES + epoxy
+DDS

NO SILICA

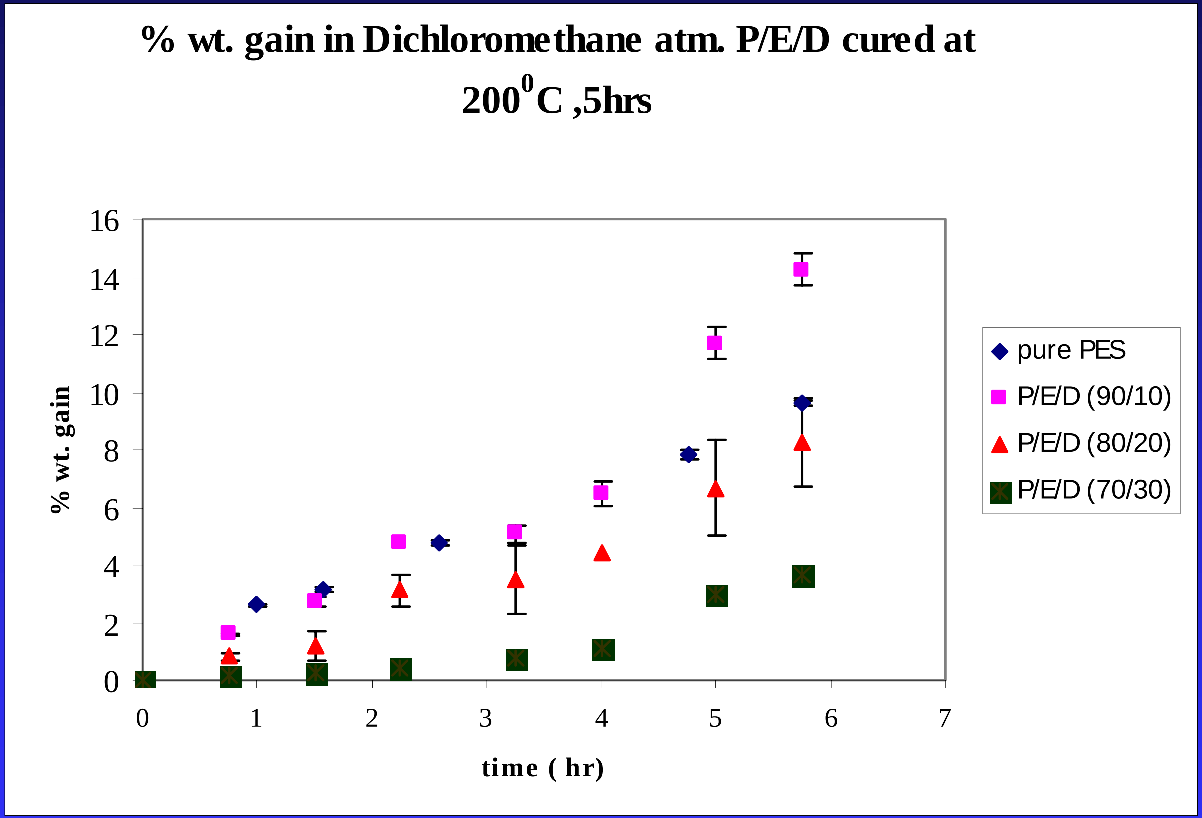


• The degree of curing in 10 and 20% epoxy cases are less than the 30% epoxy case – DILUTION EFFECTS

INCOMPLETELY CURED EPOXY INCREASES ABSORPTION

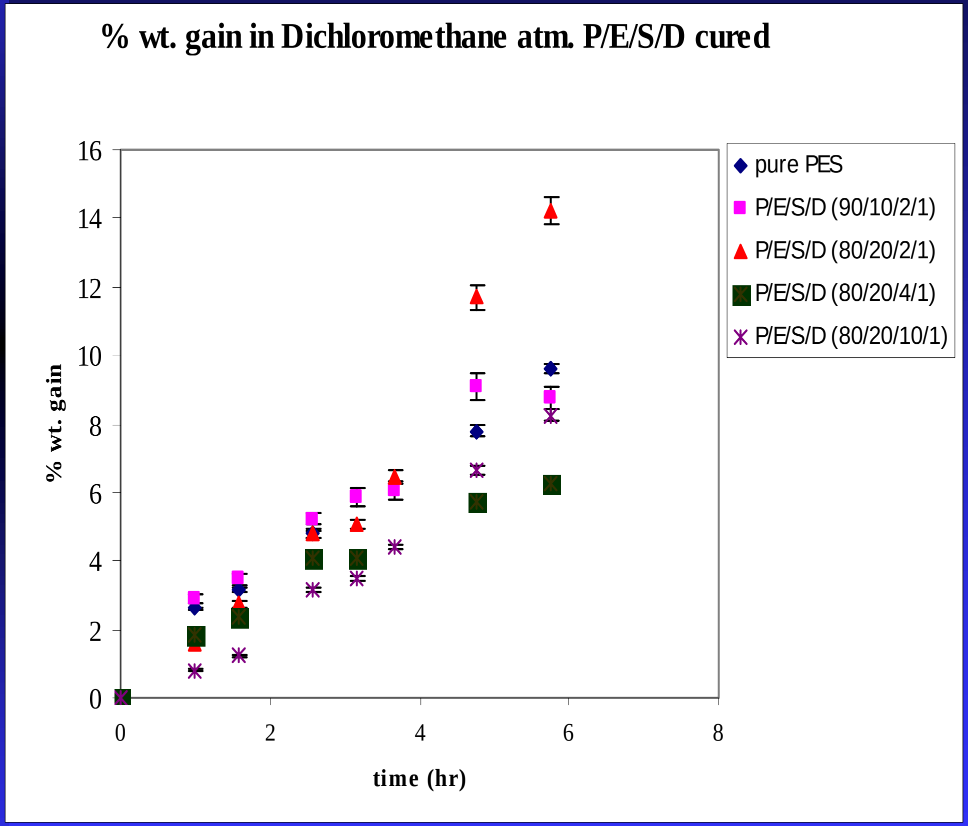
System:
PES + epoxy
+DDS

NO SILICA



• The degree of curing in 10 and 20% epoxy cases also increases with curing but still less than the 30% epoxy case – DILUTION EFFECTS

FUMED SILICA FURTHER REDUCES THE UPTAKE



- fumed silica provides better barrier to CH_2Cl_2 diffusion

SUMMARY III

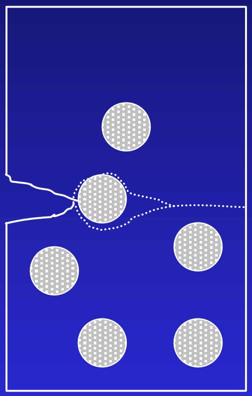
- Fumed silica increases barrier to diffusion of methylene chloride over PES, PES-epoxy systems
- Epoxy needs to be completely cured for maximum barrier properties

Thermal Properties
Heat deflection temperature

Sample	Heat Deflection Temperature °C
PES	182
PES/fumed silica(100/5)	187
PES/Epoxy/fumed silica (80/20/10) Cured at 200ºC, 3hours	206.2
PES/Epoxy/fumed silica (90/10/2) Cured at 200ºC, 4hours	206
PES/Epoxy Cured at 200ºC, 4hours	176

MECHANICAL PROPERTIES

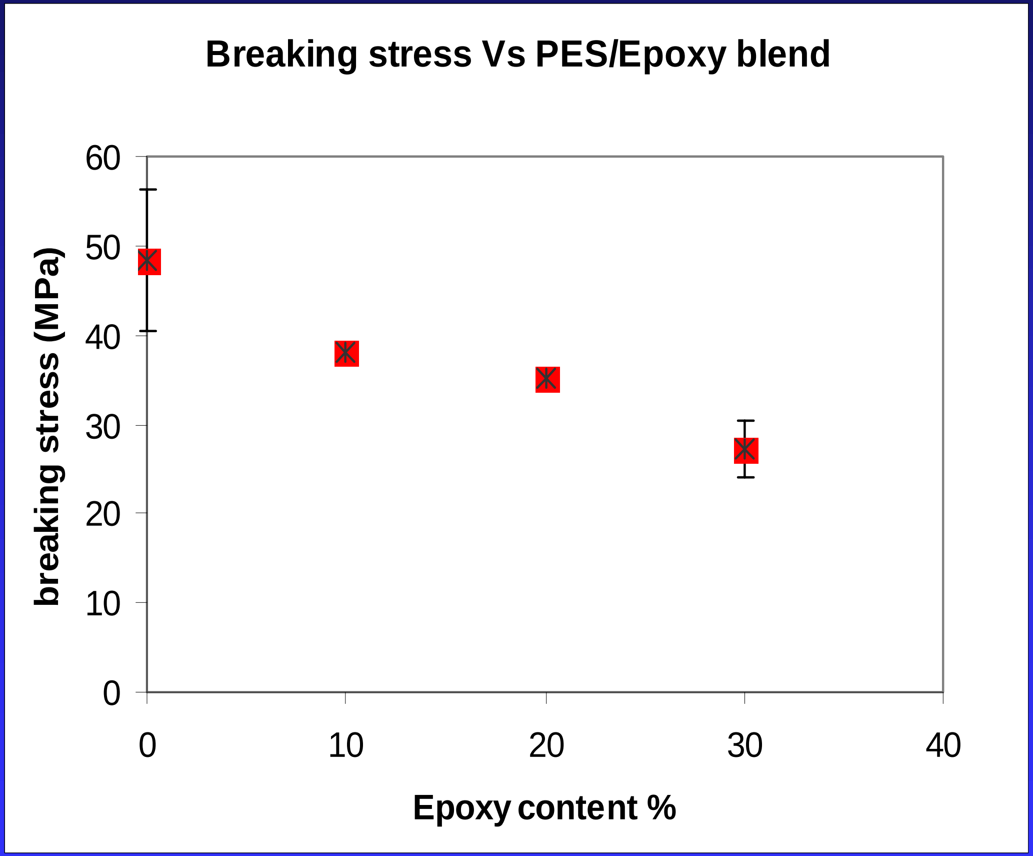
- ❑ Mechanical Properties
  - ❑ Tensile strength
  - ❑ Impact strength



✓ Fumed silica particles of almost spherical shape provides marginal improvement in mechanical properties

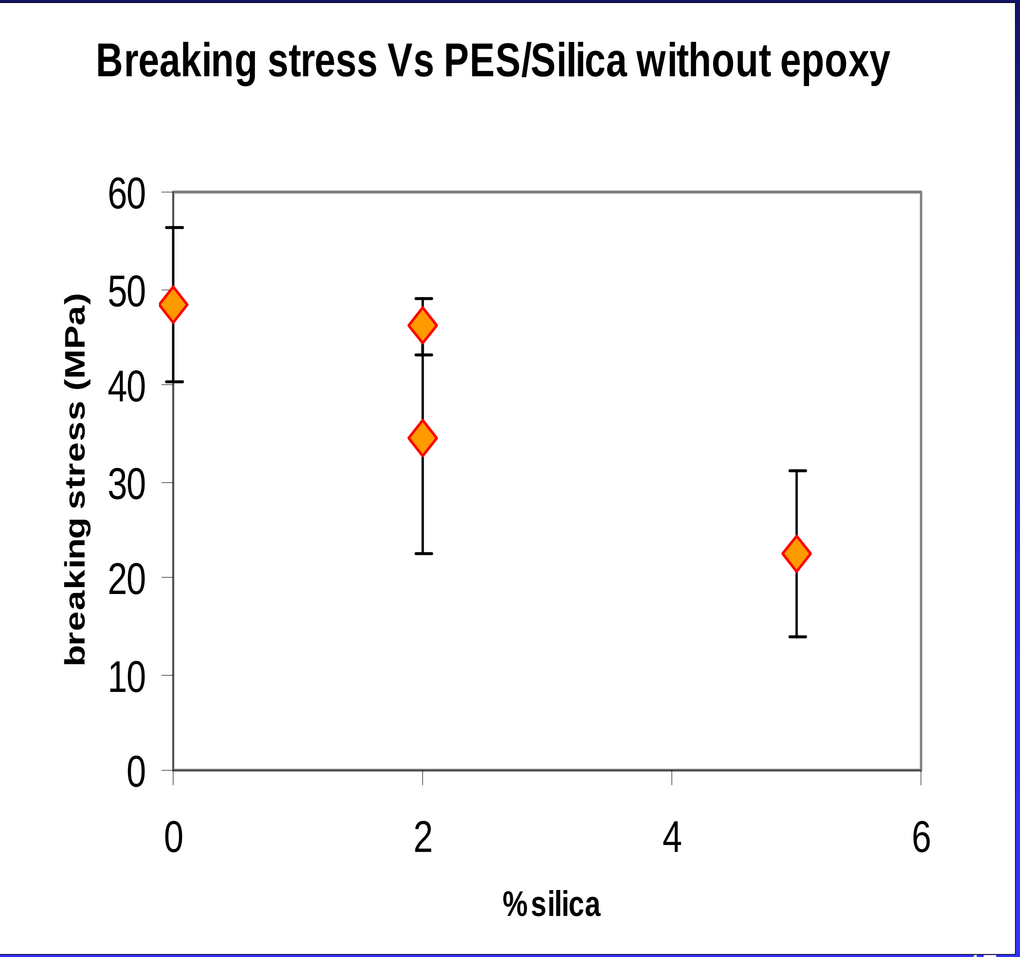
Effect of epoxy on tensile properties of PES

- Tensile strength decreases with increasing epoxy content



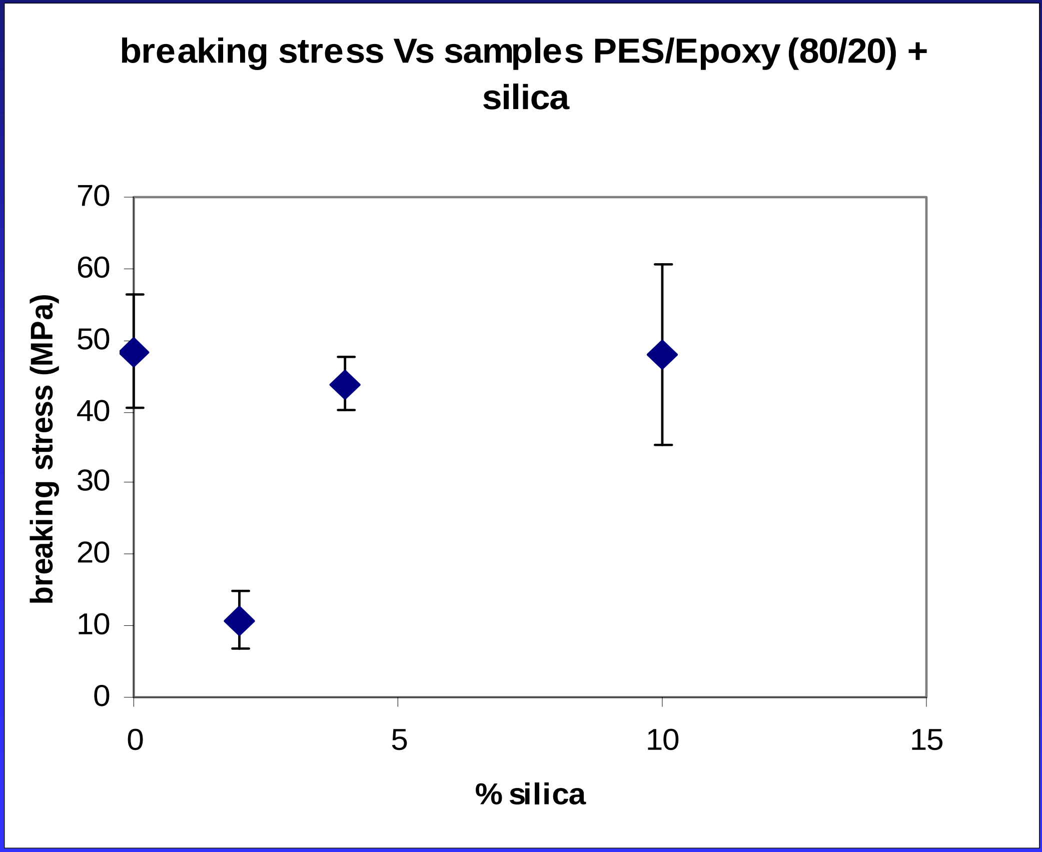
Effect of Fumed silica on tensile properties of PES

- Tensile strength decreases with increasing fumed silica content without epoxy



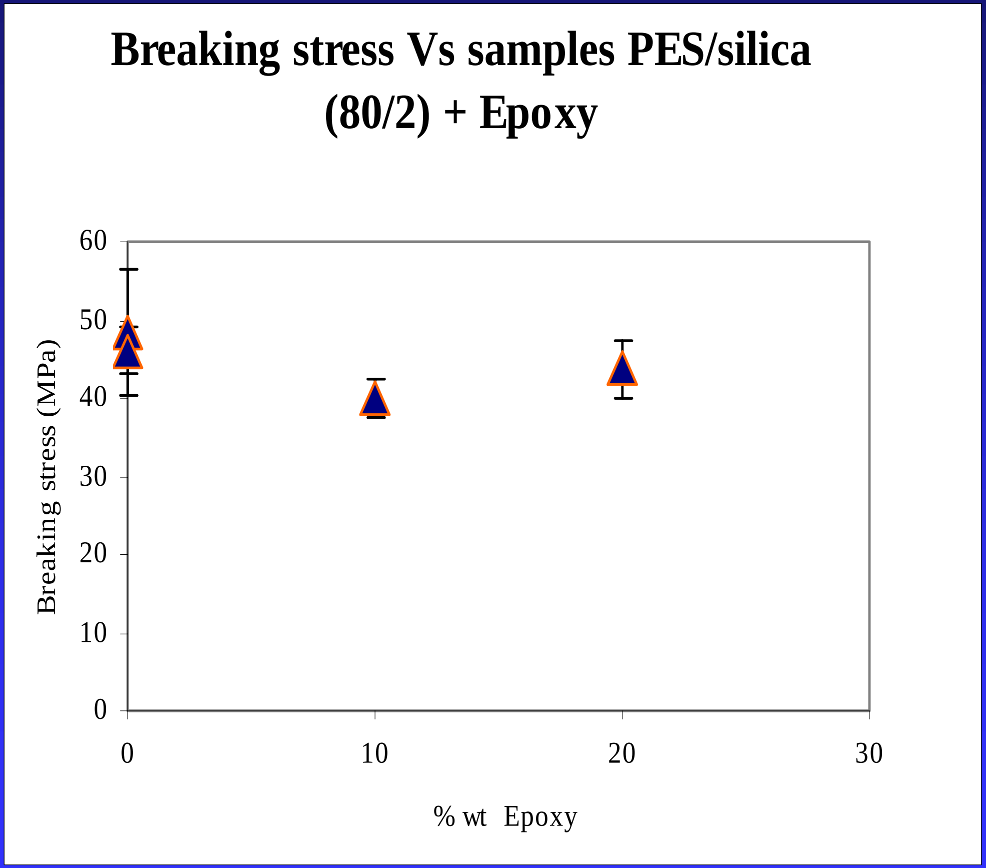
Effect of Fumed silica on tensile properties of PES in presence of epoxy

- Tensile strength recovered after curing ,even with increasing fumed silica content, in presence of 20% epoxy



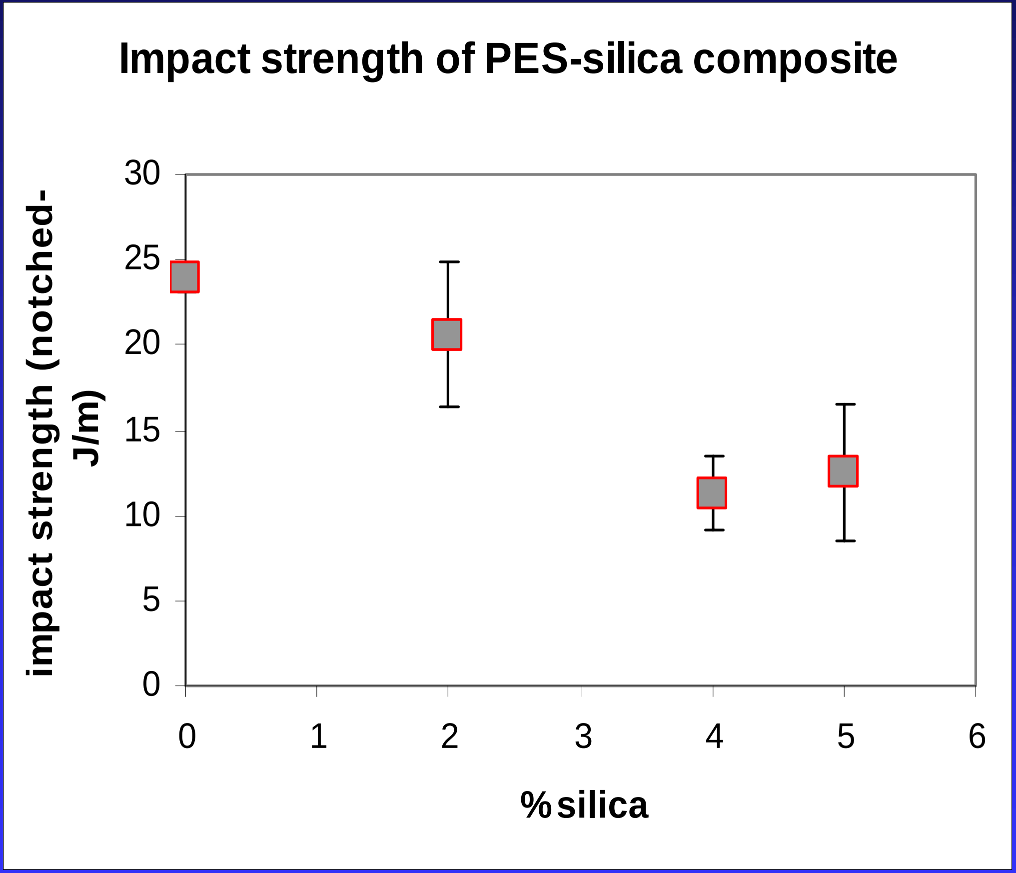
Effect of epoxy concentration with Fumed silica on tensile properties of composites

- Tensile strength recovered after curing ,even with increasing epoxy content, in presence of 2% fumed silica



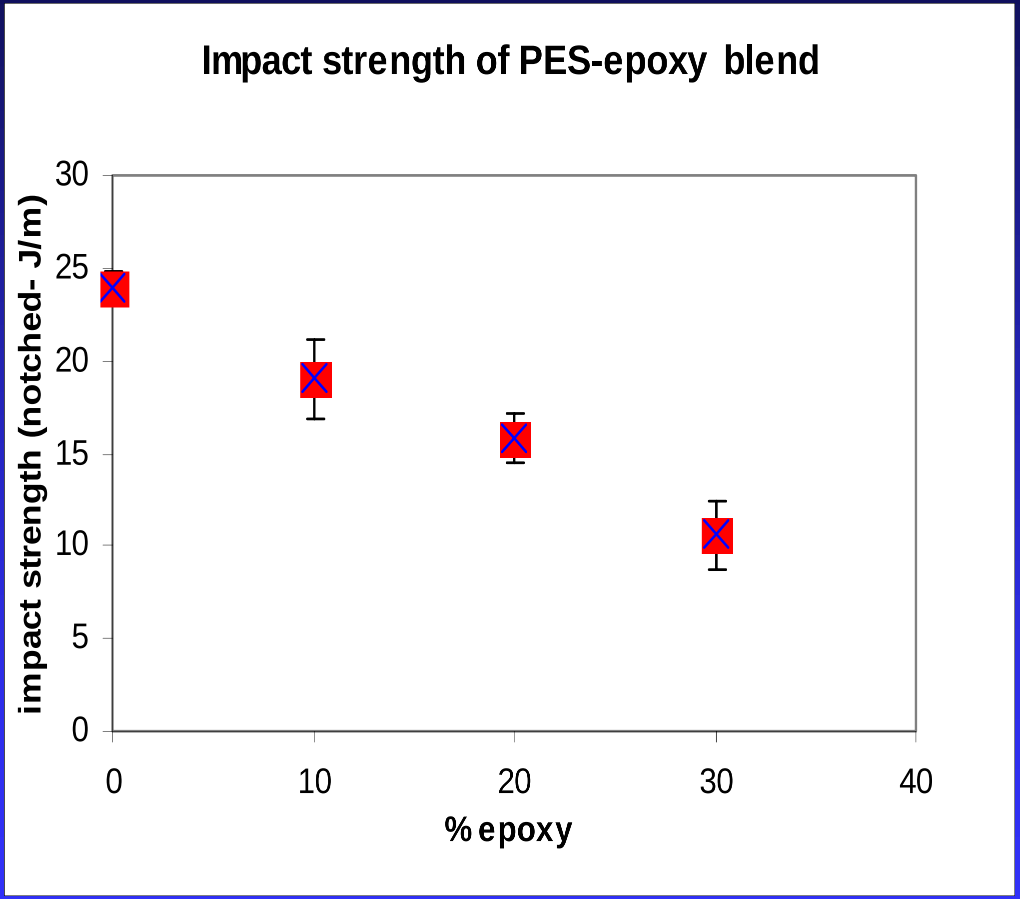
Impact strength of PES-Fumed silica

- Impact strength decreases with increasing fumed silica concentration



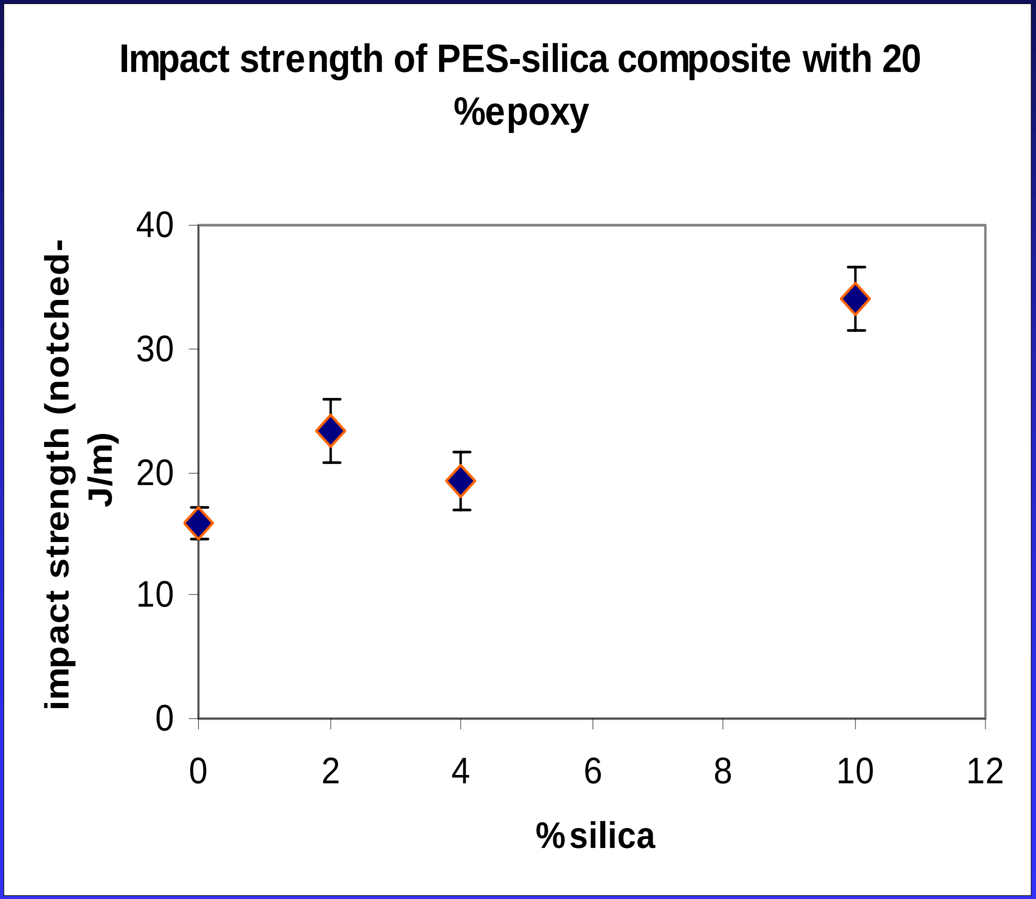
Impact strength of PES-Epoxy blend

- Impact strength decreases with increasing epoxy concentration



Impact strength of composite

- Impact strength increases with increasing fumed silica concentration



CONCLUSIONS

- Processing temperature is reduced due to addition of small amounts of epoxy
- Dispersion of fumed silica is observed to be aided by epoxy content
- Epoxy coats fumed silica particles after curing
- Epoxy may act as good dispersing agent of nanoparticles in polymers with solubility in epoxy.
- Epoxy-coated fumed silica particles reveal that nucleation of phase separation of epoxy during curing may have been triggered by polar nature of silanol groups of fumed silica
- HDT improved , mechanical properties showed marginal improvement.

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