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Photo-polymerization induced phase separation and morphology in the blends of photocurable/linear thermoplastic polymers.

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Objective

- Effect of photo-polymerization on phase separation
- Influence of processing conditions (viz. temperature, concentration etc.)
- Development of controlled morphology
- Improvement in mechanical properties
- Processing-Structure-Property-Application relationship

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Why?

- Photo polymerization is rapid yet cold curing process
- Easy and independent control over various processing parameters.
- More control over phase structures
- Strong potential for nano-composites.

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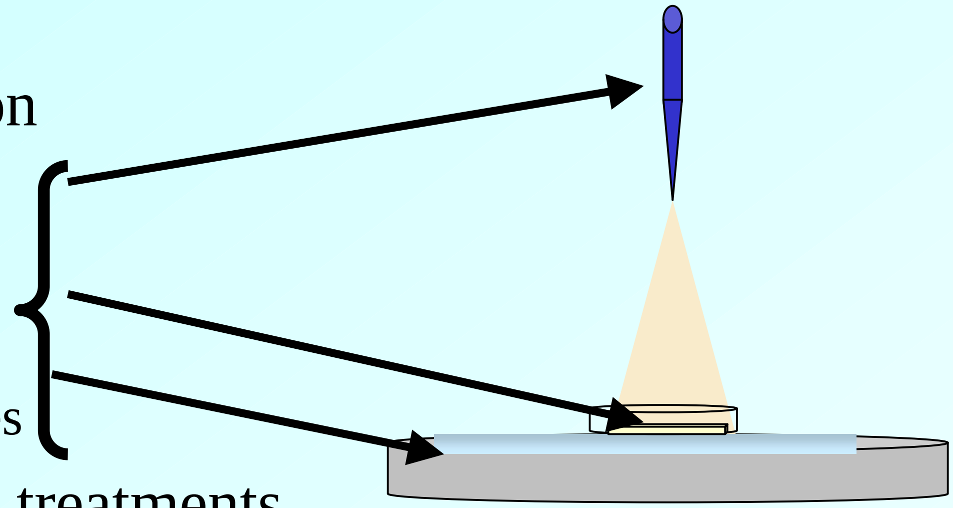
How?

- Photo polymerization
  - – UV-light curing –
  - –Concentration
  - –Temperature
  - –Independent variables



- post-polymerization treatments
  - –Annealing
  - –Freezing-in the morphology
- Second stage photo-curing
  - – increase in conversion

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What?

- **Development in morphology**
  - –SEM
  - –TEM
  - –DSC/DMTA

•**Effect of**

–chemical composition

–Annealing temperature

Curing temperature

Post-curing

On

Morphology

Mechanical properties

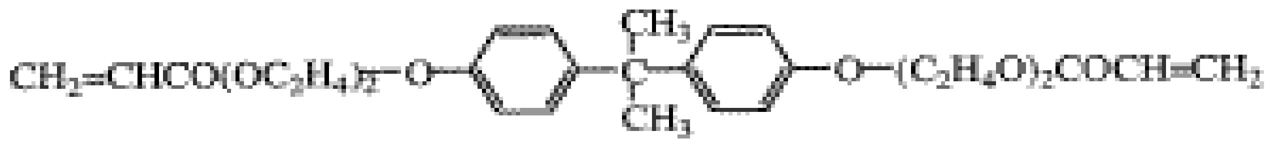
Optical properties.

Materials

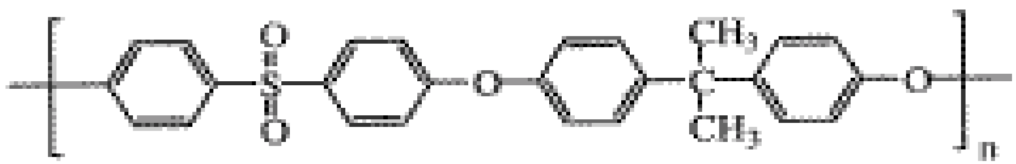
- Photocurable monomer :
  - 2,2-Bis(4-(acryloxy diethoxy)phenyl propane (BPE4)
    - Supplied by Daiichi Seiyaku Kougyo Co. Japan

- Photo initiator
  - 1-hydroxycyclohexylphenyl ketone(HCPK, Irgacure 184)
    - Supplied by Ciba specialty chemicals
- Linear thermoplastic polymer
  - Polysulfone (Udel P-307)
    - Supplied by Amoco Chemicals.

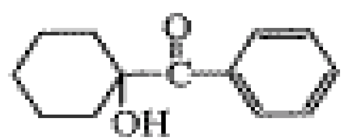
Chemical Structure of Materials



2,2-Bis(4-(acryloxy diethoxy)phenyl)propane (BPE4)



Polysulfone (PSU)



1-hydroxy cyclohexyl phenyl ketone (HCPK)

Photo-polymerization

❑ ***<u>First stage curing:</u>***

- 2wt% (0.5 mol%) HCPK was added in BPE4, BPE4/HCPK(98/2 w/w)
- Blends with various compositions
  - *Viz. for 1:1 blend, BPE4 (5g, including 2% HCPK) and PSU (5g) were dissolved in dichloromethane (80g)*
  - *Solvent cast on glass slide to make films and kept in petri dish at RT overnight.*
  - *Then dried in vacuum oven at 50C for 3 hrs.*
- Films were then heated at desired temperature and irradiated with ultraviolet(UV) light (intensity at surface ca 10mWcm-2, at 365 nm) for 90-120 sec using high pressure Hg-lamp under nitrogen atmosphere
- Films were transparent and homogenous after first step curing

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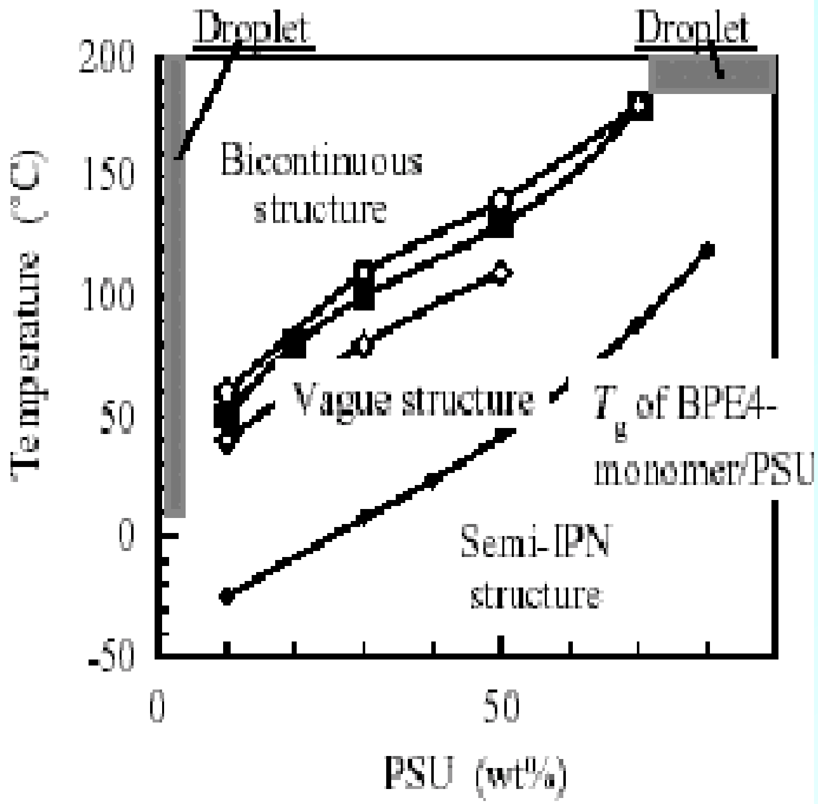
First Step cure:

Phase structure depending on polymerization conditions



- BPE4/PSU system prepared by photopolymerization with light intensities

(◊) 1mW cm^{-2} ,(■) 10mW cm^{-2} , (o)75mW cm^{-2}

- (•) T_g BPE4-monomer and PSU homogeneous mixtures (T_{go})

T_{bi} is the curing temperature at which the network like bi-continuous phase separated structure appeared

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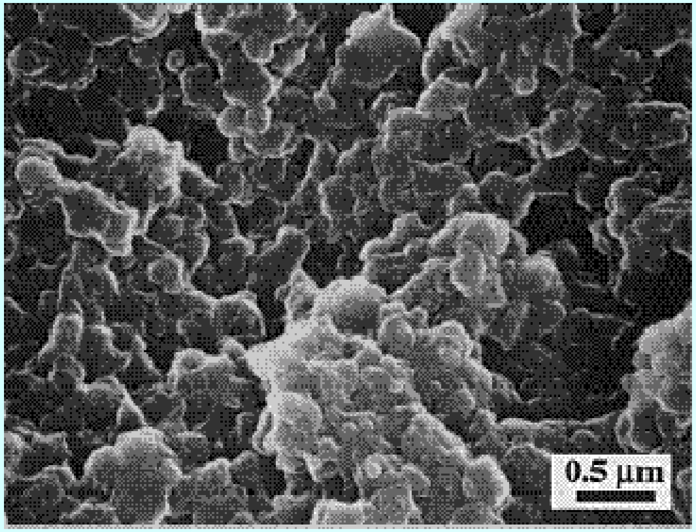
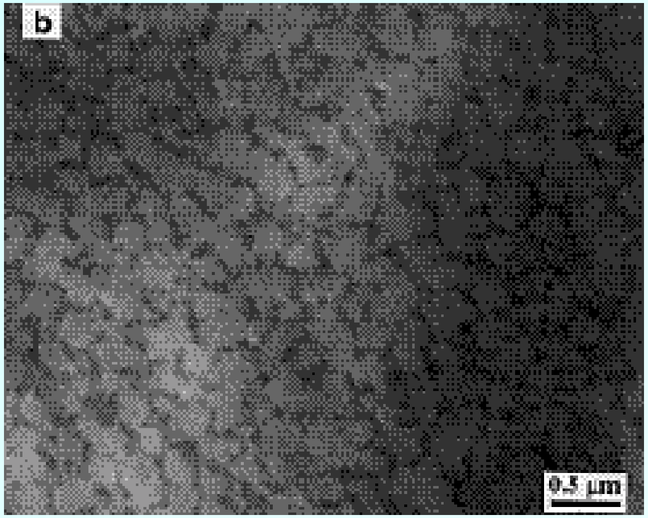
First Step cure:

Network-like bi-continuous morphology of BPE4/PSU

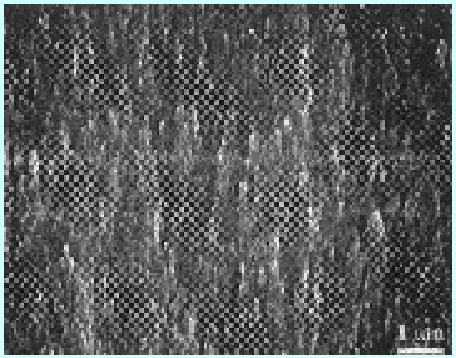




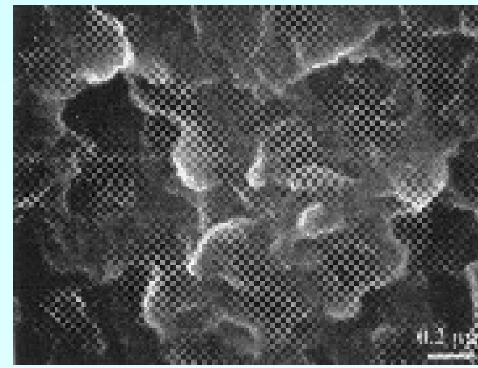
BPE4/PSU (9/1 w/w) cured at 120°C with a light intensity of 10mW cm^{-2}
(a) SEM image and (b) TEM image, in which PSU was etched out with dichloromethane

First Step cure:

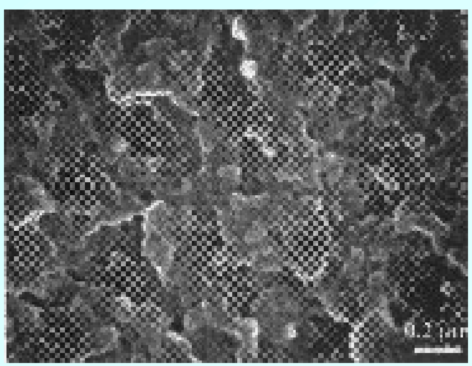
Morphology of BPE4/PSU depending on cure temperature



(a) Cured at 25°C



(b) Cured at 120°C

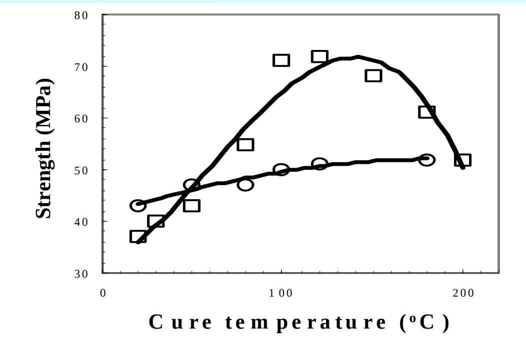


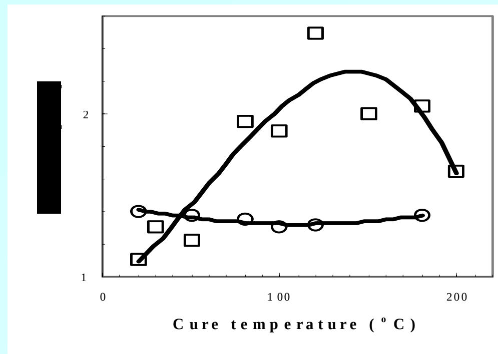
(c) Cured at 180°C

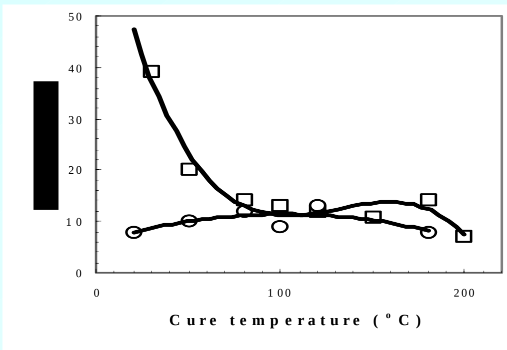
SEM micrographs of fractural surfaces after tensile test for BPE4/PSU (5/5 w/w)

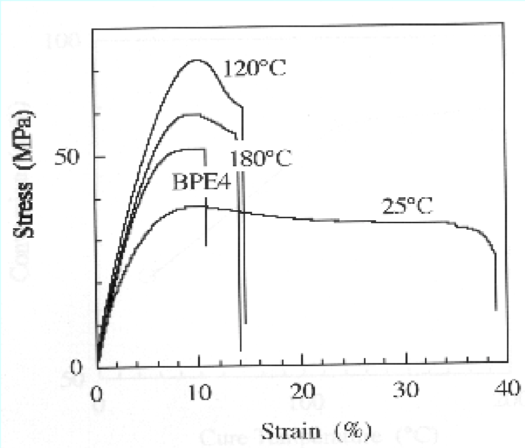
First Step cure:

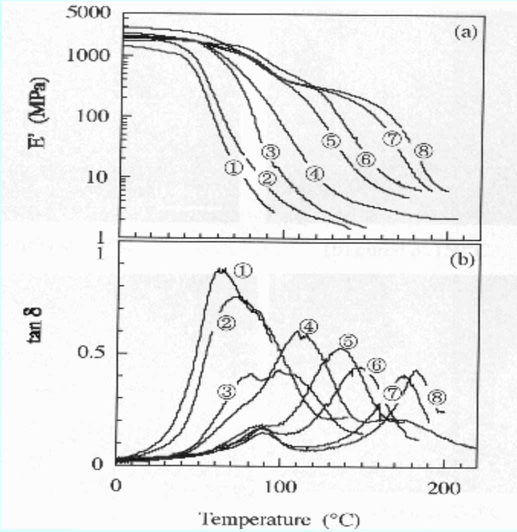
Mechanical properties of BPE4/PSU depending on cure temperature











Top:
( ) blend films of BPE4/PSU (5/5 w/w)
(°) cured neat BPE4

Bottom: BPE4/PSU (5/5 w/w)
(1) 25ºC; (2)50 ºC; (3)80 ºC; (4)100 ºC;
(5)120ºC; (6)150ºC; (7)180ºC; (8)210 ºC.

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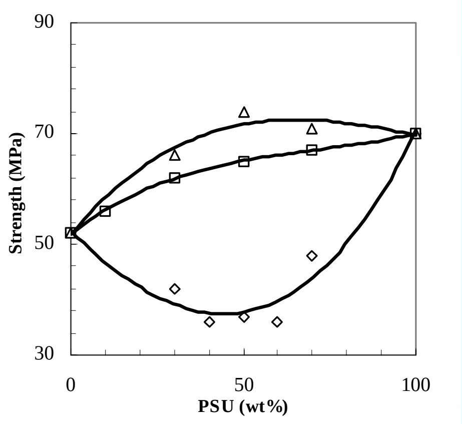
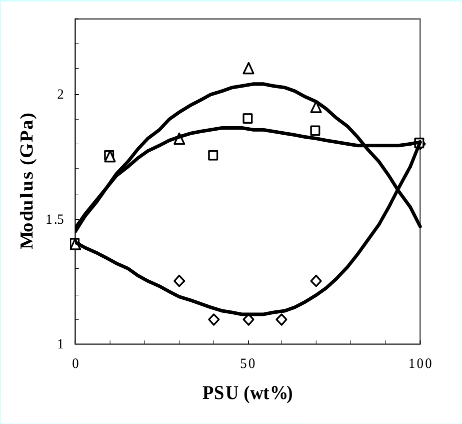
First Step cure:

Effect of cure temperature

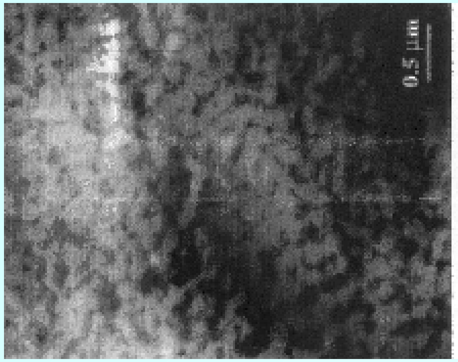
Mechanical properties of BPE4/PSU depending on composition



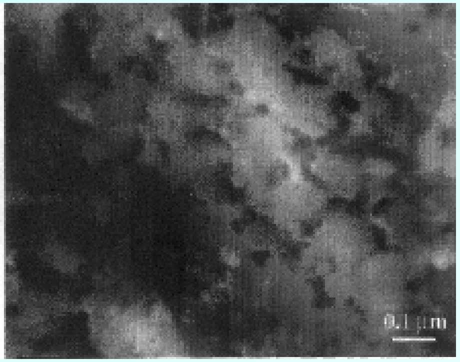


Top:Blends of BPE4/PSU
First step cure temperatures:

1.(Δ) optimum cure temperature (vague structure)
2.( ) below Tgs of the homogenous mixture of BPE4 monomer and PSU (semi-IPN structure)
3.(♦) temperature +30ºC at which network-like structure become clear.



(a)



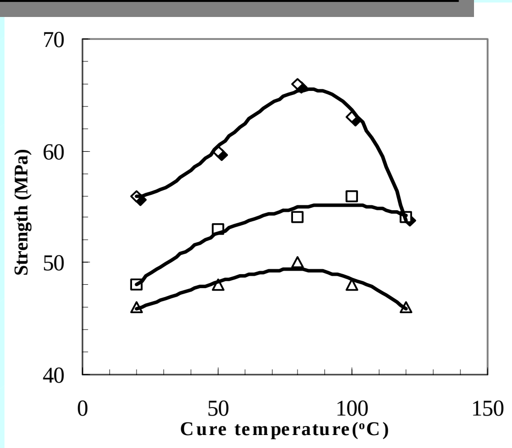
(b)

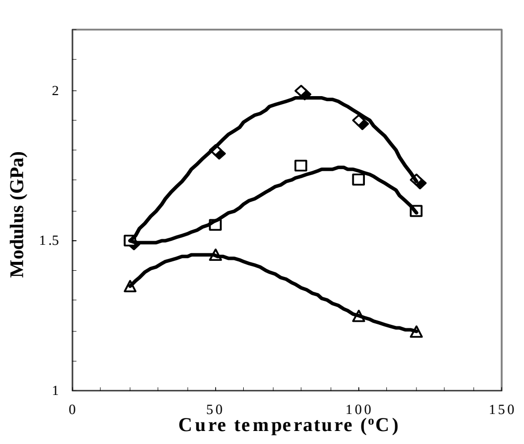
Bottom TEM images of BPE4/PSU:
(a) 10wt% PSU cured at 80ºC.
(b) 30wt% PSU cured at 110 ºC

First Step cure:

Effect of comp./temp:

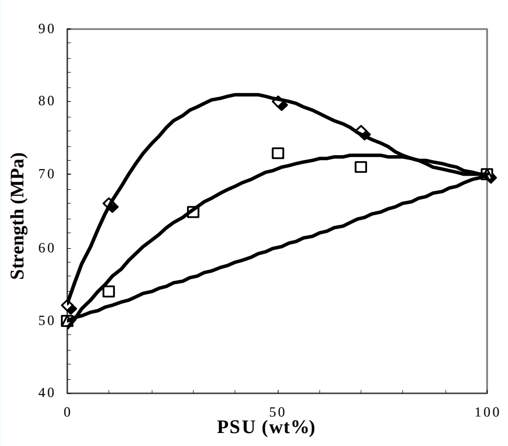
Mechanical properties of BPE4/PSU depending on irradiation intensity

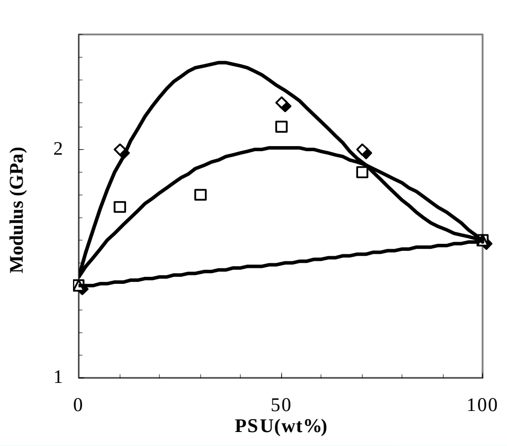




Top:Blends of BPE4/PSU (90/10 w/w)

1. (◊) 75 mW cm^{-2}
2. ( ) 10 mW cm^{-2}
3. (Δ) 1 mW cm^{-2}





Bottom: BPE4/PSU blend films cured at optimal cure temperature:

(a) (◊) 75 mW cm^{-2}.

(b) ( ) 10 mW cm^{-2}

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Annealing:

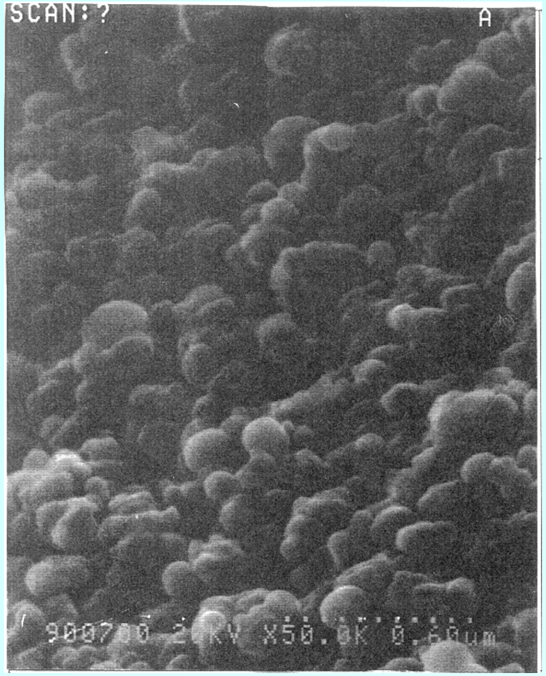
Effect of annealing

- Necessity of annealing
- Effect of annealing on morphology
- Effect of annealing on blends with semi-IPN structures
- Improvement in mechanical properties

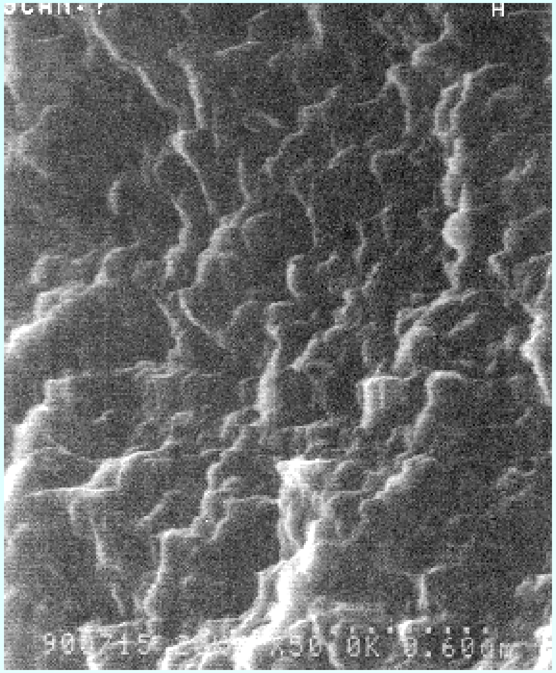
Annealing:

Effect of annealing on morphology

Why first step curing is necessary?



Annealed at 180 ºC for3 hrs and cured at 150 ºC for 3min with 75 mW cm^{-2}



First step cured at : RT, 50 mW cm^{-2} , 2min
Annealed at 180 ºC for3 hrs and post cured at 150 ºC with 75 mW cm^{-2} , for 3min

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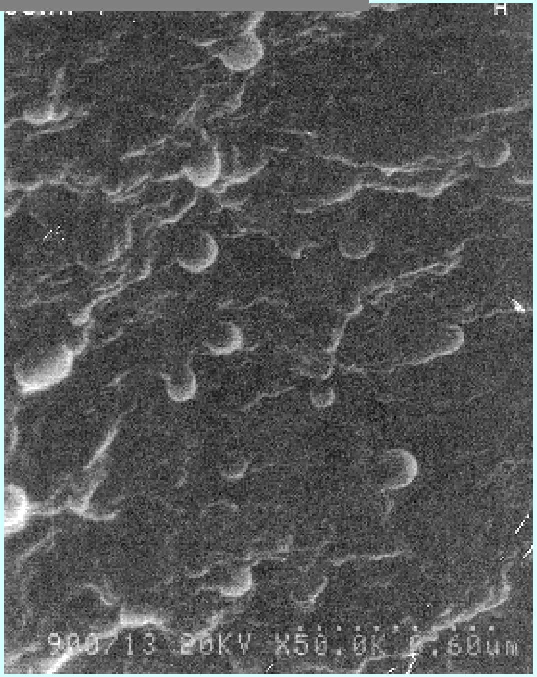
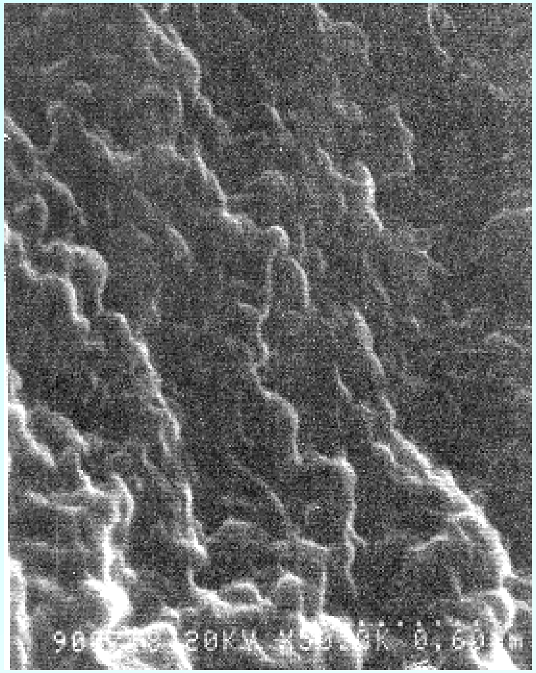
Annealing:

Effect of annealing on morphology

Why annealing is necessary?



First step cured at : RT, 30 mW cm^{-2} , 2min
No annealing and post cured
at 150 ºC with 75 mW cm^{-2} , for 3min



First step cured at : 80 ºC, 30 mW cm^{-2} , 2min
Annealed at 180 ºC for3 hrs and post cured
at 150 ºC with 75 mW cm^{-2} , for 3min

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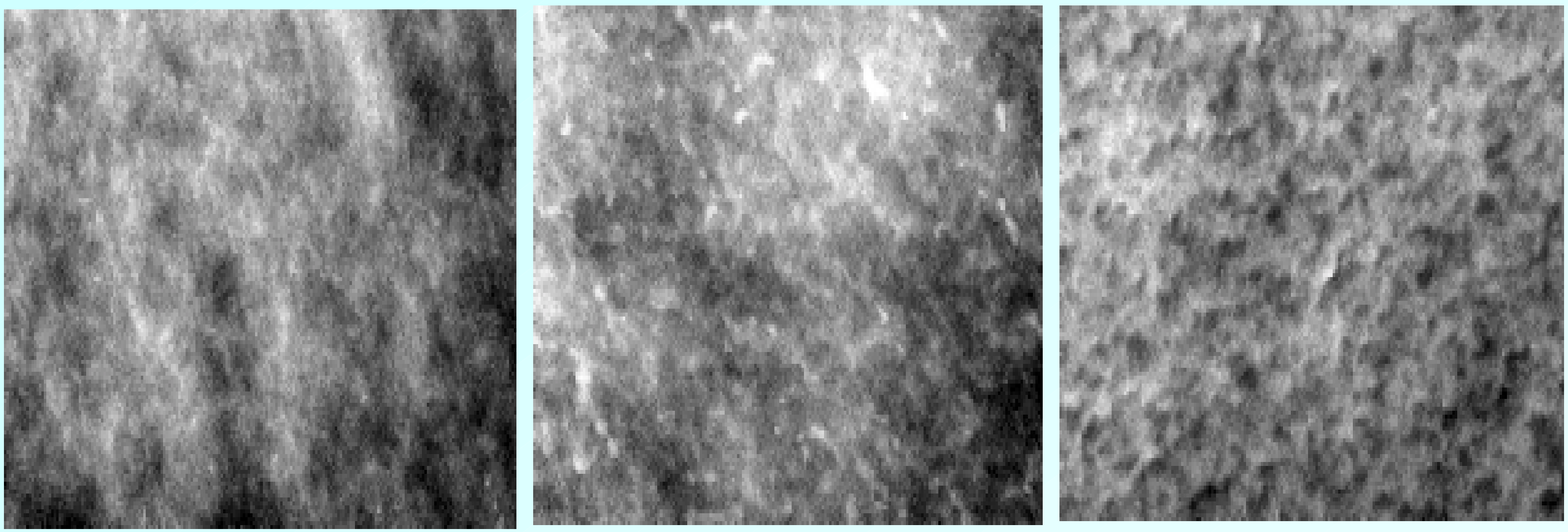
Annealing:

Effect of annealing on morphology

TEM images for BPE4/PSU blends after annealing



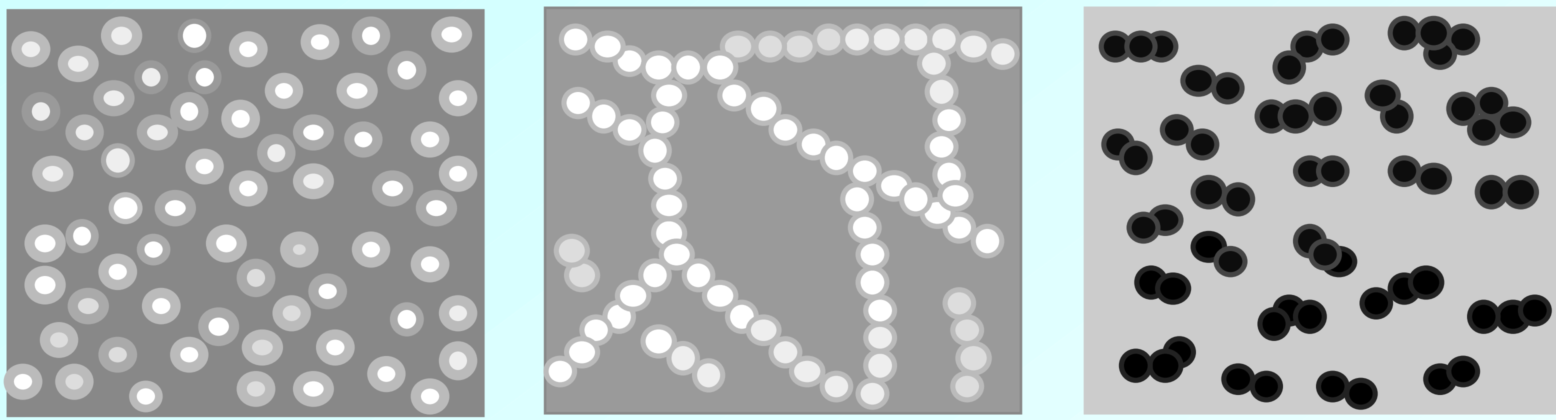
(a) annealed at 80°C (b) annealed at 150°C (c) annealed at 200°C

The blend films with semi-IPN structure were prepared by curing below T_g, and then annealed and further photo cured at optimal temperature for 90 sec. with 75 mW cm^{-2} intensity

Annealing:

Effect of annealing on morphology

Schematic phase morphology induced by annealing from semi-IPN structure



65°C **120°C** **165°C**

T_g of the blend with semi-IPN structure

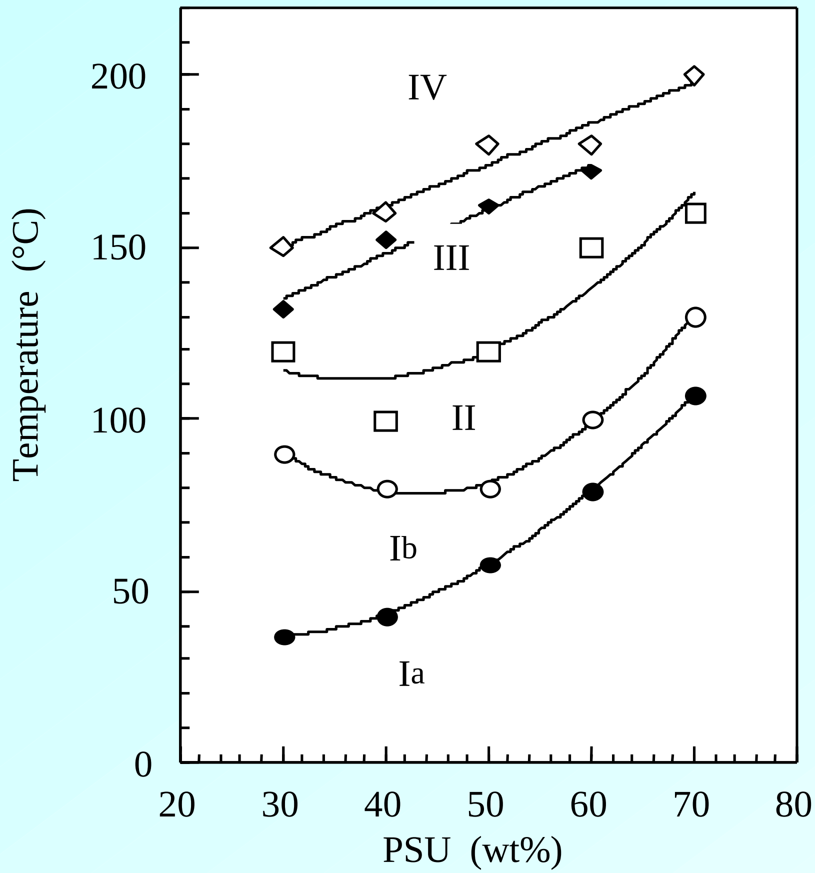
T_g of the PSU-rich phase

Annealing Temperature (°C)

The white part is the BPE4-rich phase, while the dark part is the PSU-rich phase

Annealing:

Effect of annealing on phase separated structures



IV: PSU-rich domain structure

III: Interconnected structure

II: BPE4-rich domain structure

Ib: phase separated semi-IPN structure

Ia: miscible semi-IPN structure

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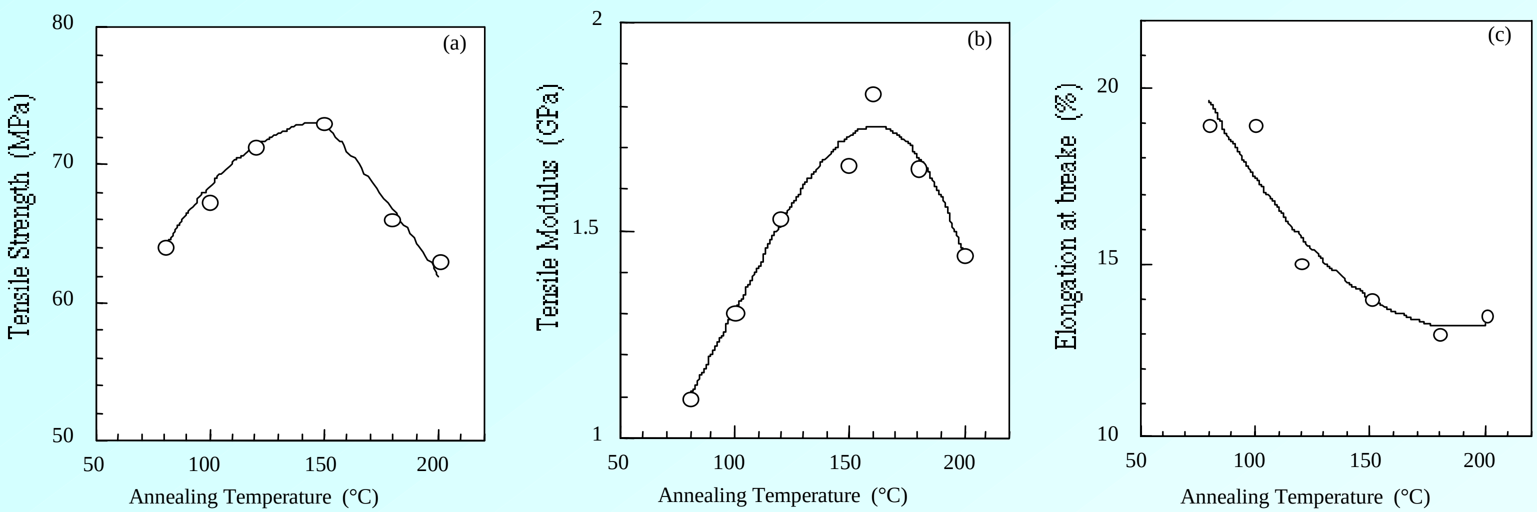
Annealing:

Effect of annealing on mechanical properties



Effect of annealing temperature on: (a) tensile strength, (b) modulus and (c) conversion of BPE4 in the blends of BPE4/PSU (5/5 w/w).

The blend film with semi-IPN structure was prepared by curing below T_g, and then annealed at the optimal annealing temperature for 1 hrs. The annealed films were additionally photo cured at optimal temperature for 90 sec. with 75 mW cm^{-2} intensity

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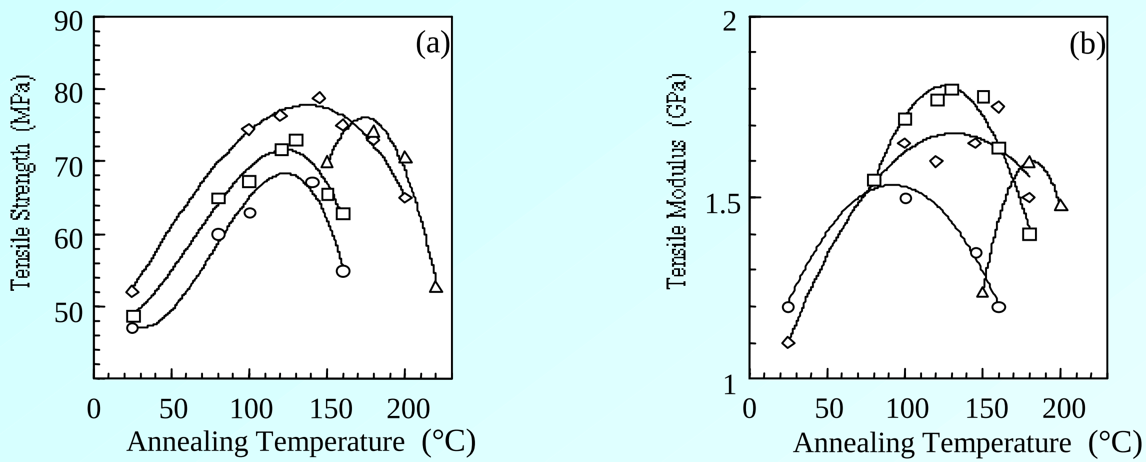
Annealing:

Effect of comp./cure temp

Effect of annealing on mechanical properties



Effect of annealing temperature on (a) tensile strength, (b) tensile modulus for BPE4/PSU

The first step cure temperature was –5°C for 30(o) and 40 (□) wt% PSU
and 24°C for 60(◊) and 70 (Δ) wt% PSU.

The post cure temperatures were130°C for 40 wt%, 160°C for 60 wt%, and 180°C for 70wt%

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Conclusions

- Photo-polymerization induces Phase separation in blends
- Step process of photo-polymerization helps in improving mechanical properties
- Various factors affects morphology of phase separated blends
  - ✓ Curing temperature
  - ✓ Intensity of UV-light -
  - ✓ Composition of blends
- Annealing proves to be an important step for property enhancement
- Three step process : First step cure, second step annealing and third step post-curing gives bi-continuous morphology with improved mechanical properties.

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