Polymer additives

Introduction

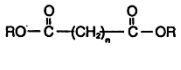
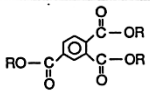
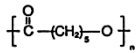
- Many polymer products cannot be used without additives
- The uses of lubricant, plasticizer, processing aid, impact modifier and stabilizer in PVC are the examples.

สารเคมี	หน้าที่การทำงาน	ปริมาณ (pph)
พอลิไวนิลคลอไรด์ (เกรดแขวนลอย, ค่า K-value = 66 (SG660) จากบริษัท Thai Plastic and Chemicals Co. Ltd. (TPC)	Polymers	100
DOP	Plasticizers	50
Acrylic rubber (AR71)	Impact modifier	5
กรดสเตียริค (Stearic acid)	External Lubricant	0.3
เบนโซไธเอโซล (Benzothiazole) (ชื่อการค้า Tinnuvin P)	UV absorber	~ 0.3-0.5
Tinuvin 833 XT	UV stabilizer	0.5
Sufur/ soap	Vulcanizing agent	1/10
สารประกอบเชิงซ้อนของโลหะแบเรียม แคดเมียม และซิงค์ (Ba-Cd-Zn salts) (ชื่อการค้า CS – 1368 N)	Thermal Stabilizer	2.5 – 3.0
สารประกอบอินทรีย์เชิงซ้อนของโลหะแบเรียมแคดเมียมและซิงค์ (ชื่อการค้า CR-01 บริษัท Cosmos Chemical Co., Ltd) สภาพเป็นผง	(Co-stabilizer)	0.5
ยางอะคริลิคนาโน Narpow VP-301	Toughening agent	
ยางอะคริลิคนาโน Narpow VP-362	Toughening agent	

Common plasticizers for PVC

- Dialkyl phthalate
- Aliphatic diester
- Trialkyl phosphate
- Trialkyl trimellitate
- Polycaprolactone

Table 1. Chemical structures of some plasticizers for PVC.

Plasticizer	Chemical structure
Dialkyl phthalate	
Aliphatic diester	
Trialkyl phosphate	
Trialkyl trimellitate	
Polycaprolactone	

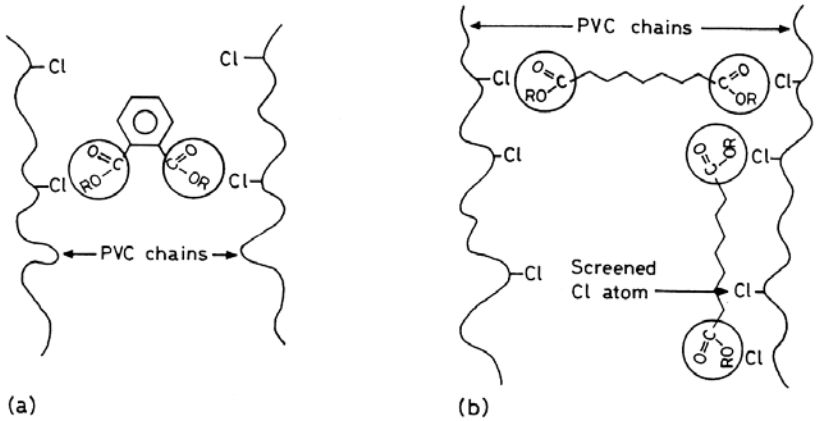


FIG. 1.31 Action of (a) a polar aromatic plasticizer and (b) a polar aliphatic plasticizer on PVC chains.

- Increasing MW of the plasticizer through the use of polymeric plasticizer may lead to an increase in performance due to higher transition temperature of the plasticizer

- Polar aliphatic plasticizers mix less well with PVC than do the polar aromatic and, consequently may exude (bloom) from the plasticized polymer more easily.

Anti-plasticization effect

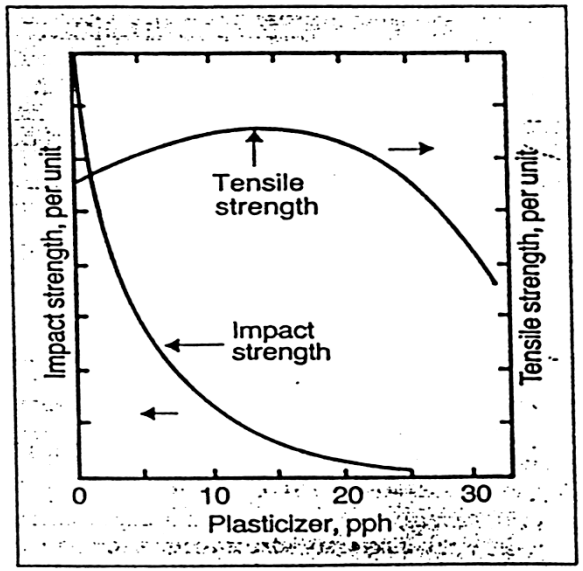


Figure 3. Effect of TCP concentration on the impact and tensile strength of plasticized PVC is shown.

Anti-plasticization effect occurring at low plasticizer content.
This may be associated with an increase in degree of crystallinity of PVC, owing to increased mobility of PVC molecules

Plasticizers for PLA

US patent 2006/0045940 A1

- Polyalkylether
- Polyesters
- Glycerol
- Glycerol triacetate,
- Glycerol tripropionate
- Lactic acid

US Patent 6,121,410

- Alkyl citrates e.g. triethyl citrate

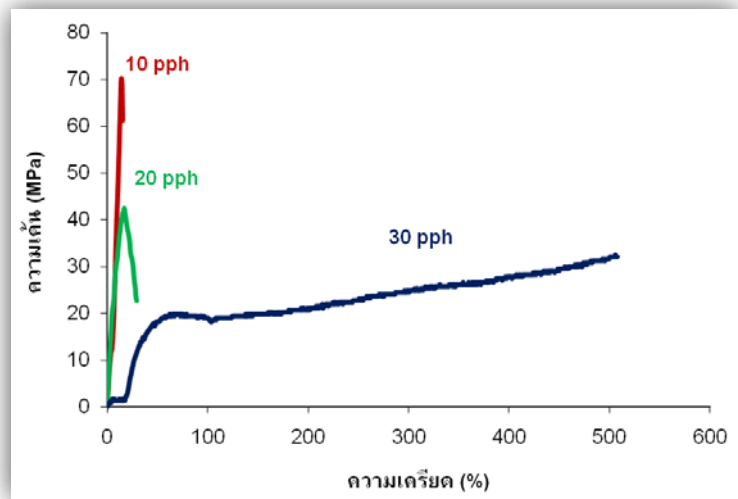
US patent 5,498,650

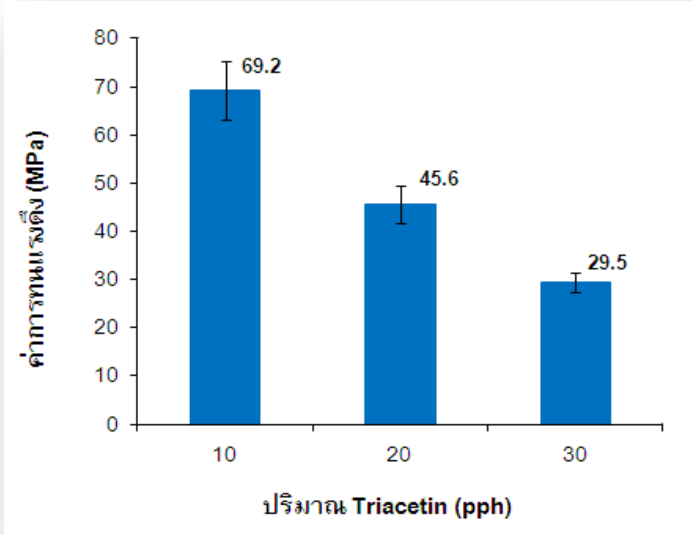
- Epoxidized soybean oil

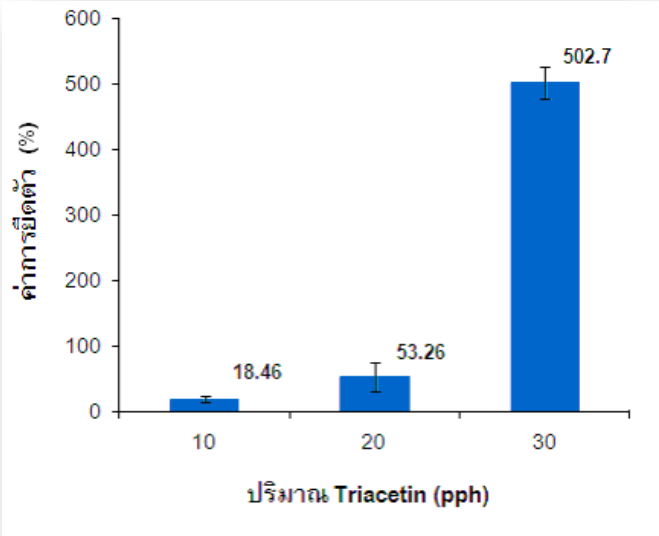
Some FDA approved Plasticizers (food grade)

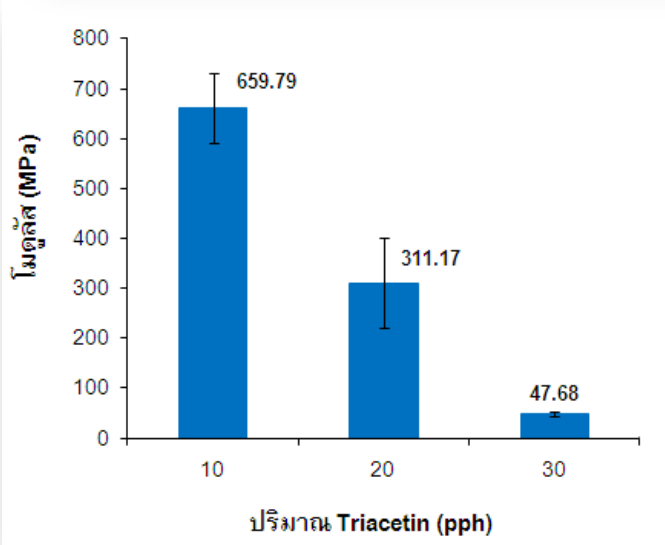
- **PBOH** [Poly(1,3-butanediol)]
- **DBS** [Dibutyl sebactae]
- **AGM** [Acetyl glycerol monolaurate]
- **PEG** [Poly(ethyleneglycol)]
- **DOA** [Di-2Etylhexyl Adipate]
- **Triacetin plasticizers** e.g. glycerol triacetate
- Epoxidized soybean oil

การเปลี่ยนแปลงค่าสมบัติทางกลของ PLA ตามปริมาณสาร triacetin







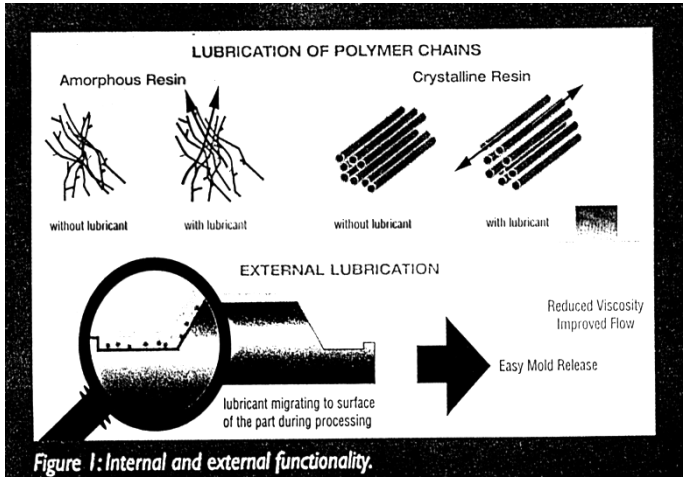


ค่า Tg ของ PLA ที่ผสมพลาสติไซเซอร์ในปริมาณต่าง ๆ

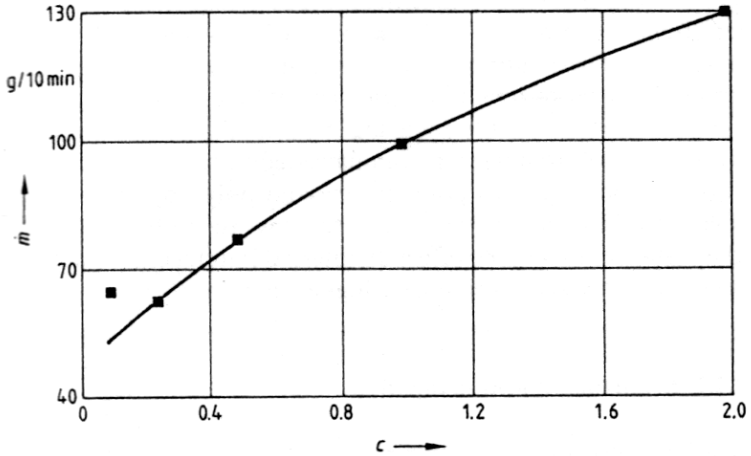
Sample	T_g (°C)
PLA 2002D	64.25
PLA + Triacetin (10 pph)	47.55
PLA + Triacetin (20 pph)	42.30
PLA + Triacetin (30 pph)	34.46

Lubricants

- There are 2 types of lubricant, depending on the solubility in polymer
- Internal lubricant
  - Reduced molecular interaction and viscosity, improved flow
- External lubricant
  - Lubricant migrate to surface of the part during processing
  - Easy mold release



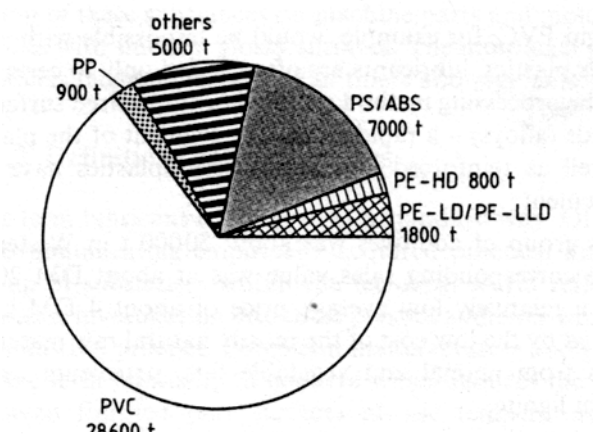
Plastics Additives & Compounding *January 2001*



Increase in output rate as a function of distearyl phthalate concentration in PVC (high pressure capillary viscometer, nozzle: 10mm/1mm; pressure: 340 bars; temperature: 190 degree C

Why using (internal) lubricant ?

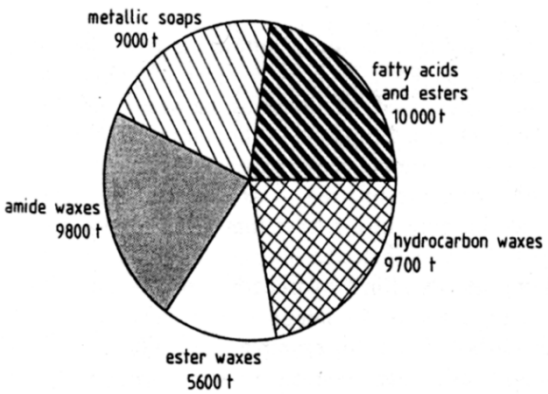
- Flow-ability of thermoplastic melts cannot be increased as desired by raising temperature.
- Thermal stability of polymer molecules are limited and if these are exceeded, discoloration, chain scission, cross-linking may result.
- On the other hand, by selecting low molecular weight of polymer in order to promote the flow-ability, some mechanical properties such as toughness, HDT, might be loss.
- For this reason lubricants are required.



Lubricant consumption by type of plastic (Western Europe 1985).

Types of Lubricant

Types of lubricant	Examples
Fatty acids	Stearic acid
Fatty acid esters of glycerol and other short chain alcohols (ester waxes)	Glycerol monooleate, butyl stearate
Fatty alcohols and their carboxylic acid esters	Stearyl alcohol, distearyl phthalate
Metallic soap	Calcium stearate, Zinc stearate, lead stearate
Polyolefin waxes (hydrocarbon waxes)	PE wax (Mw ~ 2000-9000)
Polar polyethylene waxes	EVA copolymer (Mw ~ 3500)
Fatty aciid amides (amide waxes)	Oleic acid amide



Lubricant consumption by product group (Western Europe 1985).

Impact modifier

Rubber toughened styrene based polymers

- PS + polybutadiene = HIPS
- SAN + polybutadiene = ABS
- Prepared via an *in situ* polymerization
  - maximizes the volume fraction of the rubbery phase, thus enhancing the impact toughness without causing reduction in modulus.

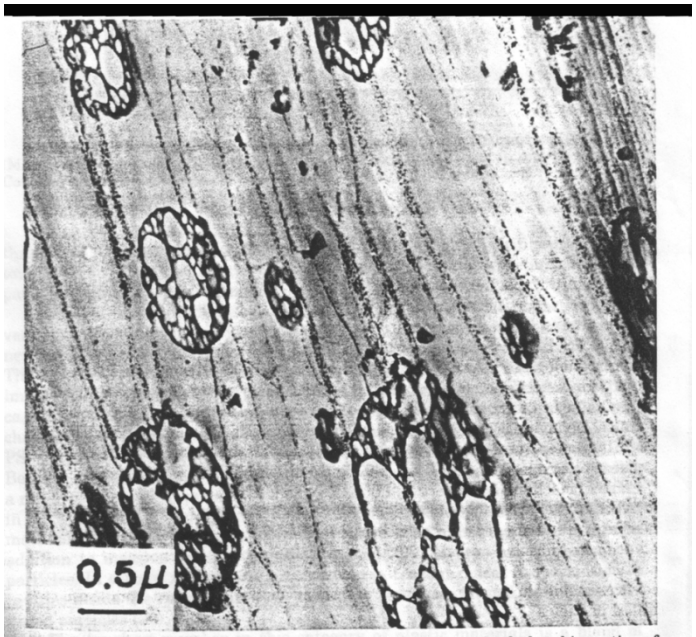


Fig. 19. Electron micrograph of an osmium tetroxide-stained ultrathin section of HIPS. This micrograph shows the typical morphology of the dispersed rubber particles. The thin lines connecting the particles are crazes formed after the material has undergone deformation.

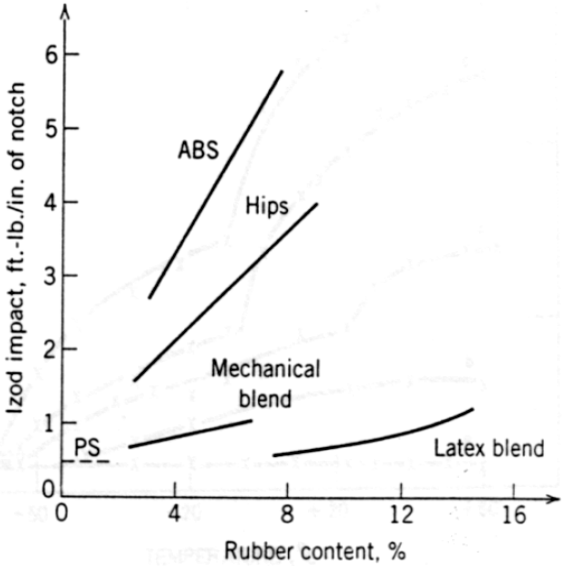


Figure 8.9 Impact resistance of several elastomer-containing styrenics. Commonly, polystyrene homopolymer has an impact resistance of around 0.3–0.4 ft-lb/in. of notch, lower left.

Some commercial impact modifiers for PLA

Trade Name	Manufacturers	Chemistry of the materials	Suitable Content	Comments
Biostrength®130	Arkema	Core-shell particle		Impact modifier (Transparent)
Biostrength®150	Arkema	Core-shell particle		Impact modifier (Opaque)
Biostrength 700	Arkema	Acrylic copolymer	4 %	•Melt strength enhancer •Transparency is maintained
Biomax®Strong 100	DuPont	Ethylene copolymer		Impact modifier for PLA. Non-food packaging
Biomax®Strong 120	DuPont	Ethylene copolymer		Impact modifier for PLA Food packaging
EMforce®Bio		Specialty mineral		Impact modifier
Paraloid [BPMS250]	Rohm and Haas	Acrylic polymer	2 % (or more)	•No effect on film clarity •FDA and EU (Directive2002/72/EC) approved

Impact modifiers for PVC

Impact modifiers for rigid PVC may be classified into 3 classes:

1. Grafted particulate rubbery polymers such as
   - methacrylate-butadiene-styrene (MBS) (clear)
   - Acrylate-methacrylate (All acrylic) (opaque)
   - Acrylonitrile-butadiene-styrene (ABS)

2. Partially miscible polymers such as
   - Nitrile rubber
   - Chlorinated PE
   - Ethylene-vinyl acetate (EVA)

3. Inorganics such as stearic acid-coated calcium carbonate

Noteworthy, Most of toughening agents are rubber. But that was not always the case.

PVC toughened with MBS particles

- MBS modifiers are grafted polymers prepared by polymerizing MMA in the presence of polybutadiene or SBR rubber.
- These polymers are then melt blended with PVC to improve impact strength
- MBS (as well as ABS-) modified PVC contain unsaturated butadiene rubber and undergo major loss of impact and suffer severe color development during outdoor aging.

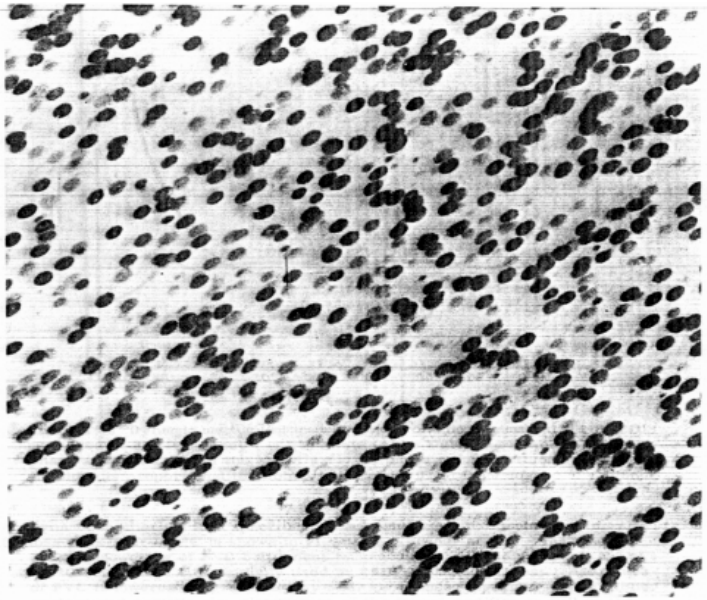
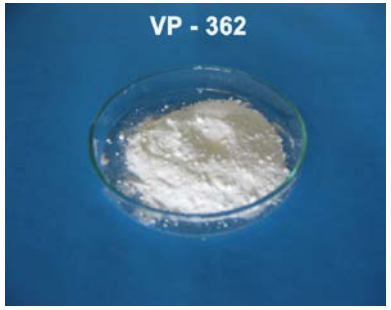


FIGURE 12 Transmission electron photomicrograph (×50,000) of well-dispersed MBS impact modifier in PVC, using OsO_5 for staining the rubber particles.

Optical properties of 12 phr MBS compound	
Light transmission (%) ASTM D-1003	87-89
Haze (%) ASTM D-1003	3-4
Yellowness index (ASTM D-1925)	3-5

Fully vulcanized nano-rubber powder

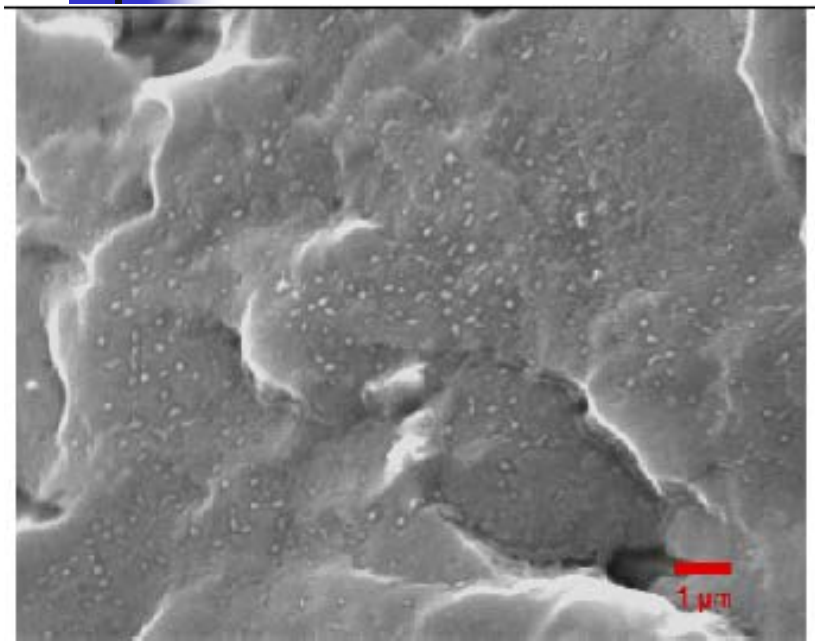
- nanosized fully vulcanized acrylic rubber powder (SINOPEC VP-301)
- Transparency of the PVC film can be maintained

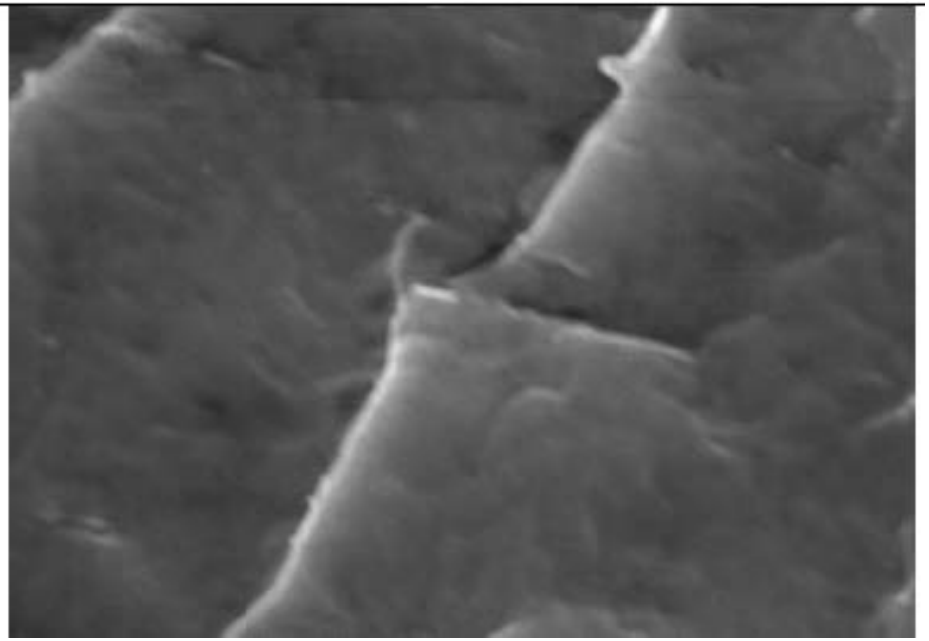


Nano acrylic rubber powder

ลักษณะของแผ่นชีทพีวีซีผสมยาง narpow (VP-301) ในปริมาณ 5 pph

ภาพถ่ายจุลทรรศน์อิเลคตรอนของแผ่นชีทพีวีซี





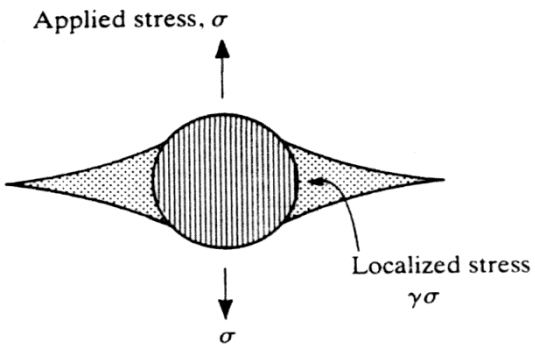
PVC + Narpow VP-301

(170 ^{o}C, 100 rpm)

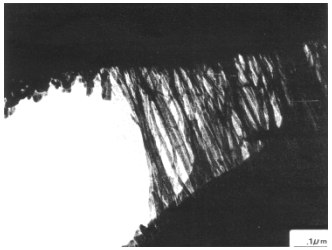
PVC ปกติ (ที่ไม่เติมยาง)

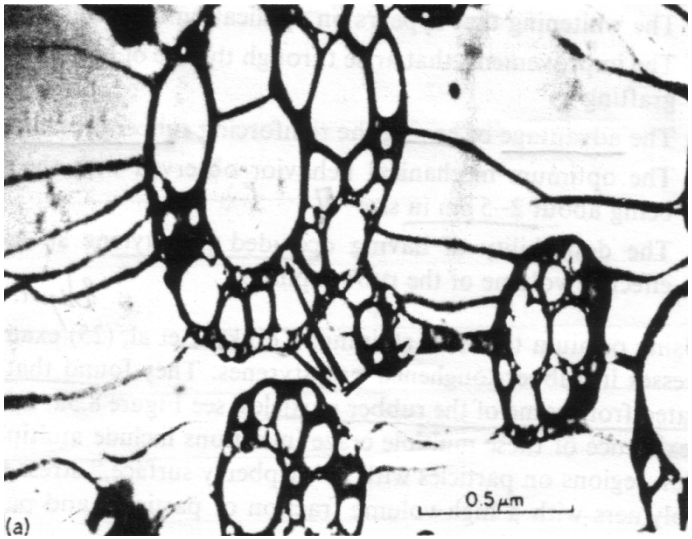
Toughening mechanisms

- Rubber deformation
- Crazing (particle induce stress concentration followed by crazing)
- Multiple crazing (particles also act as craze terminator, prevent cracking)



Stress concentration effect of a spherical rubber particle, in a rigid matrix placed under a tensile stress σ





Transmission electron micrograph of crazing and fracture in HIPS.

Factor affecting toughness

- Rubber content
- Rubber particles size
- Modulus of the rubber phase
- Distance between particles
- Interfacial adhesion between rubber particles and matrix

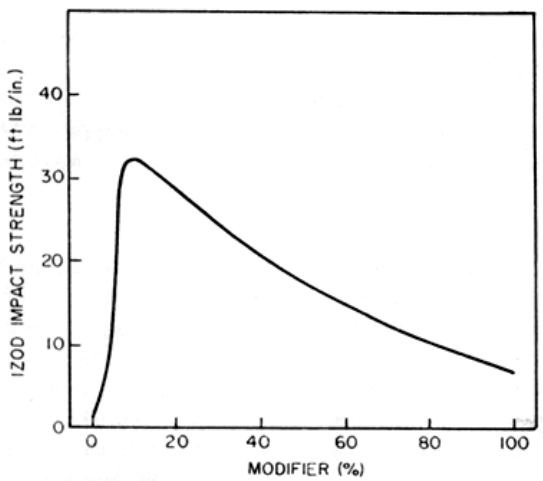


Fig. 4 Plot of Izod impact strength for PVC versus concentration of methacrylate–butadiene–styrene modifier, Acryloid KM-611 of Rohm & Haas Co. (Data from Petrich [23].)

Effect of acrylic rubber (AR) content on tensile properties of PVC/AR blend

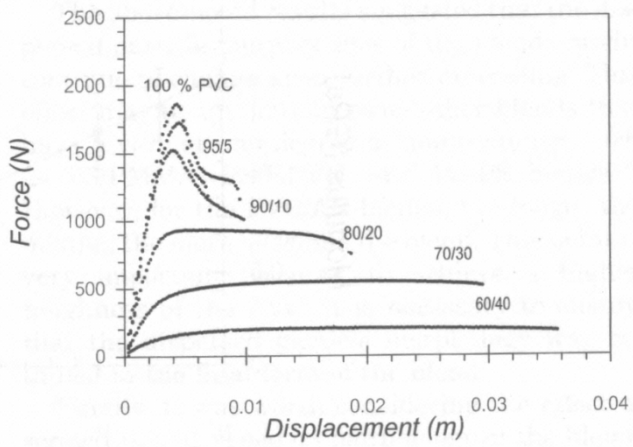


Figure 7 Force-displacement traces of PVC/AR blends at various compositions. The blending temperature was 155°C.

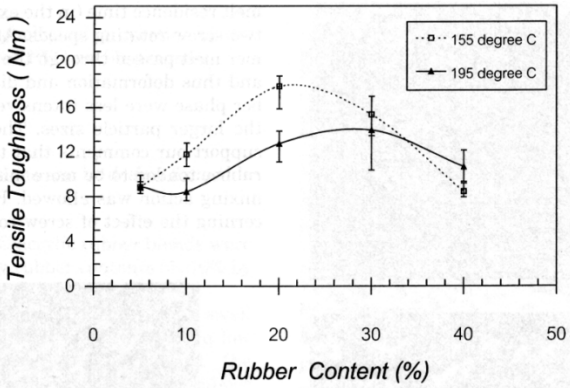
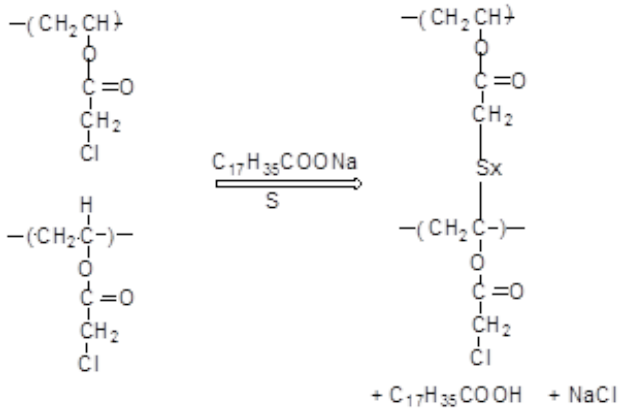


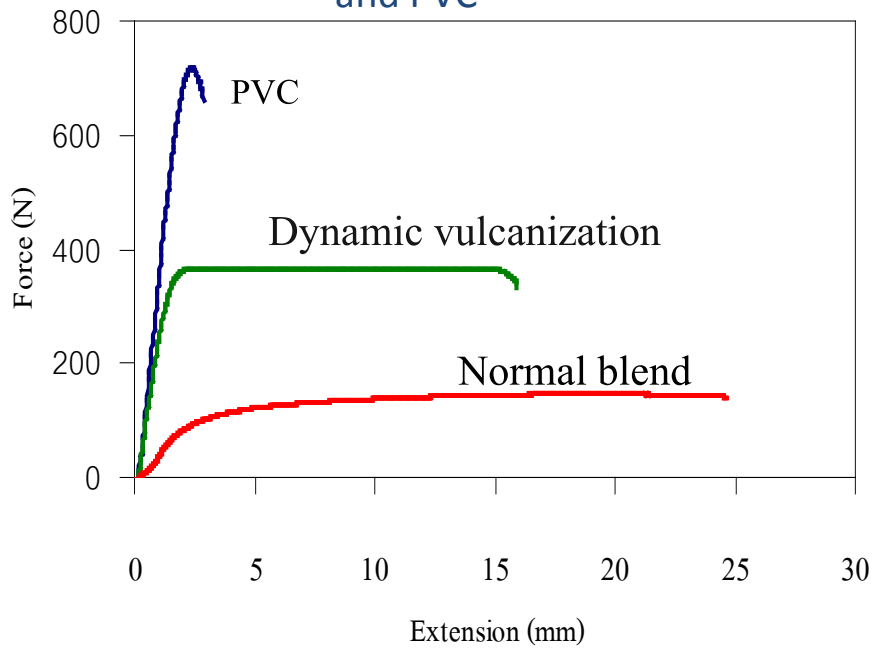
Figure 10 Tensile toughness of PVC/AR blend as a function of rubber content and temperature

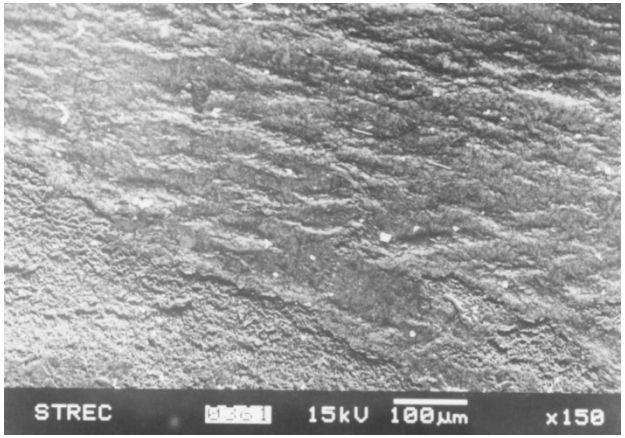
- Acrylic rubber.
  - Saturated molecules
  - Polar group, tend to be miscible with PVC
  - No compatibilizer need (unlike MBS)
  - Can be further cured to enhance properties

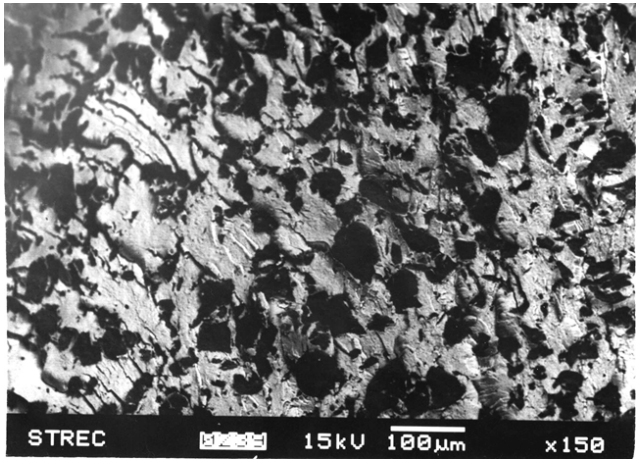
Dynamic vulcanized PVC/AR



Force-displacement traces of PVC/ACM blends (70/30) and PVC

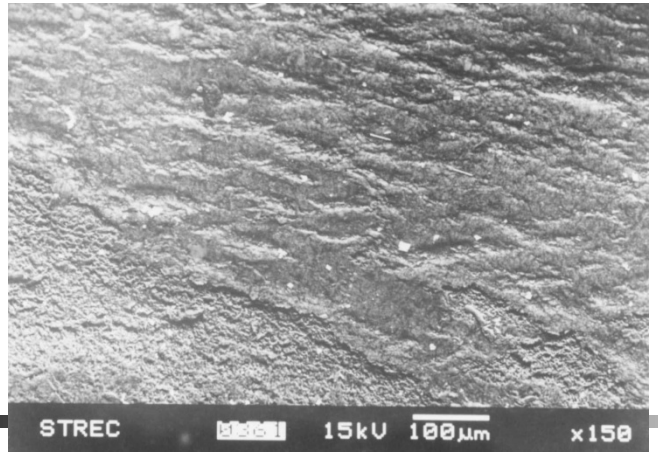




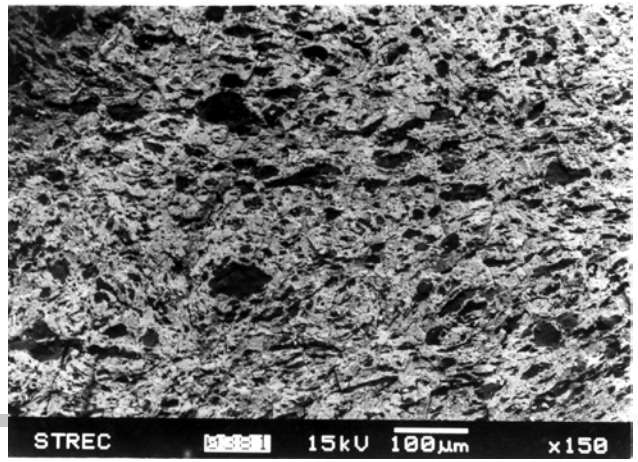


Dynamically vulcanized blend

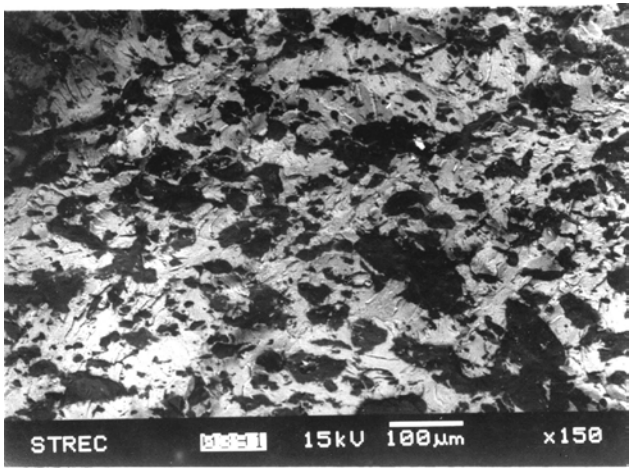
SEM micrographs of PVC/ACM (70/30) with a variety of sulfur contents



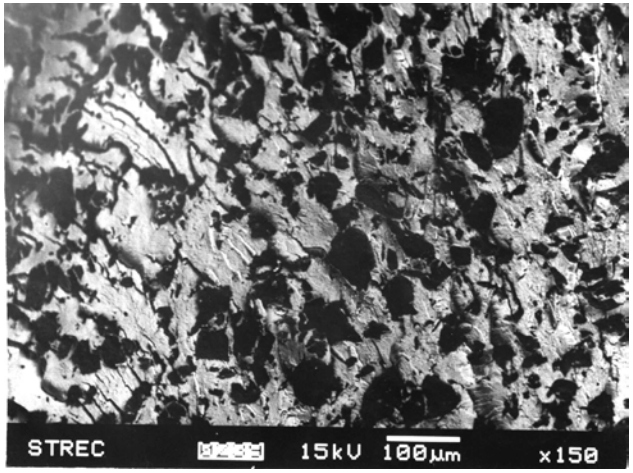
Sulfur 0 %



Sulfur 0.25 %

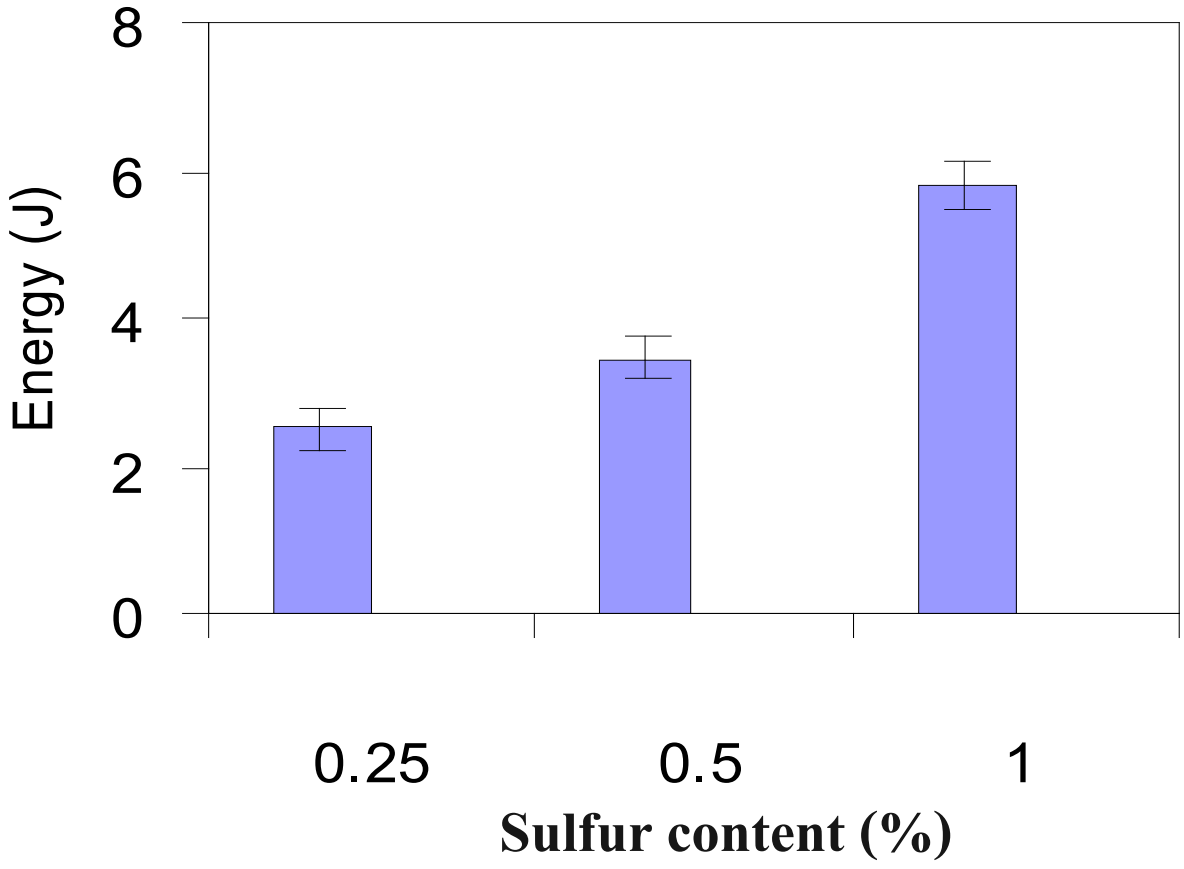


Sulfur 0.5 %

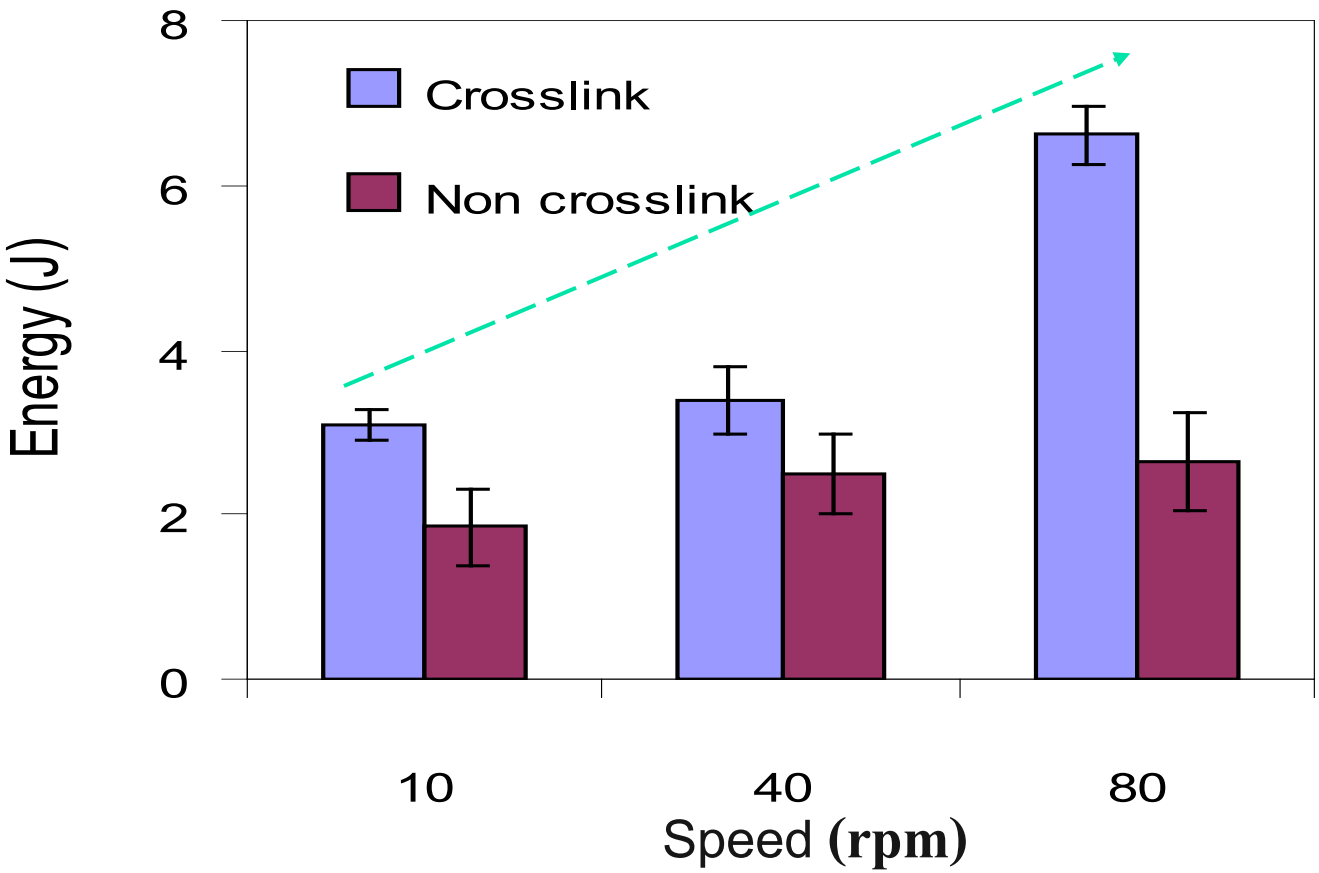


Sulfur 1.0 %

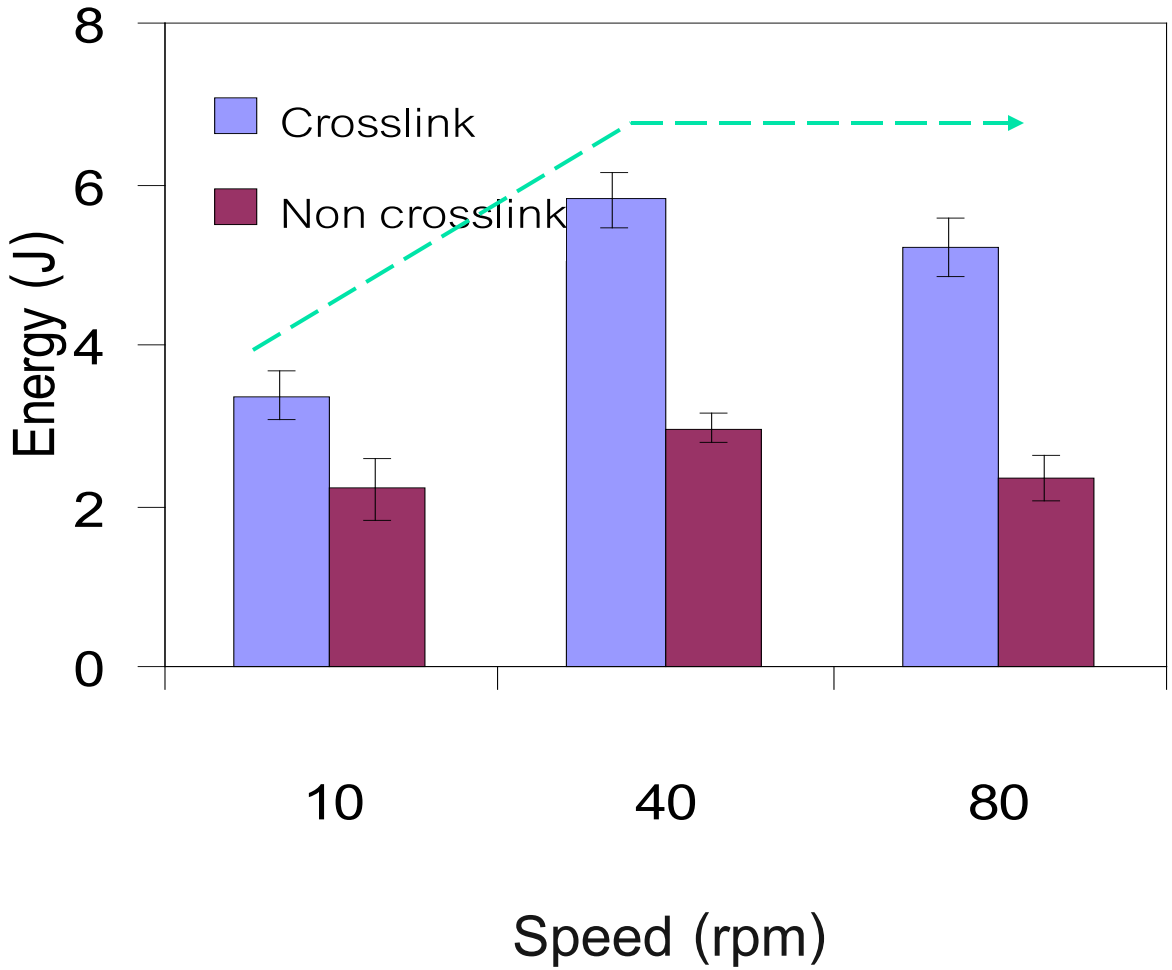
Tensile toughness of PVC/ACM (70/30) with a variety of sulfur content



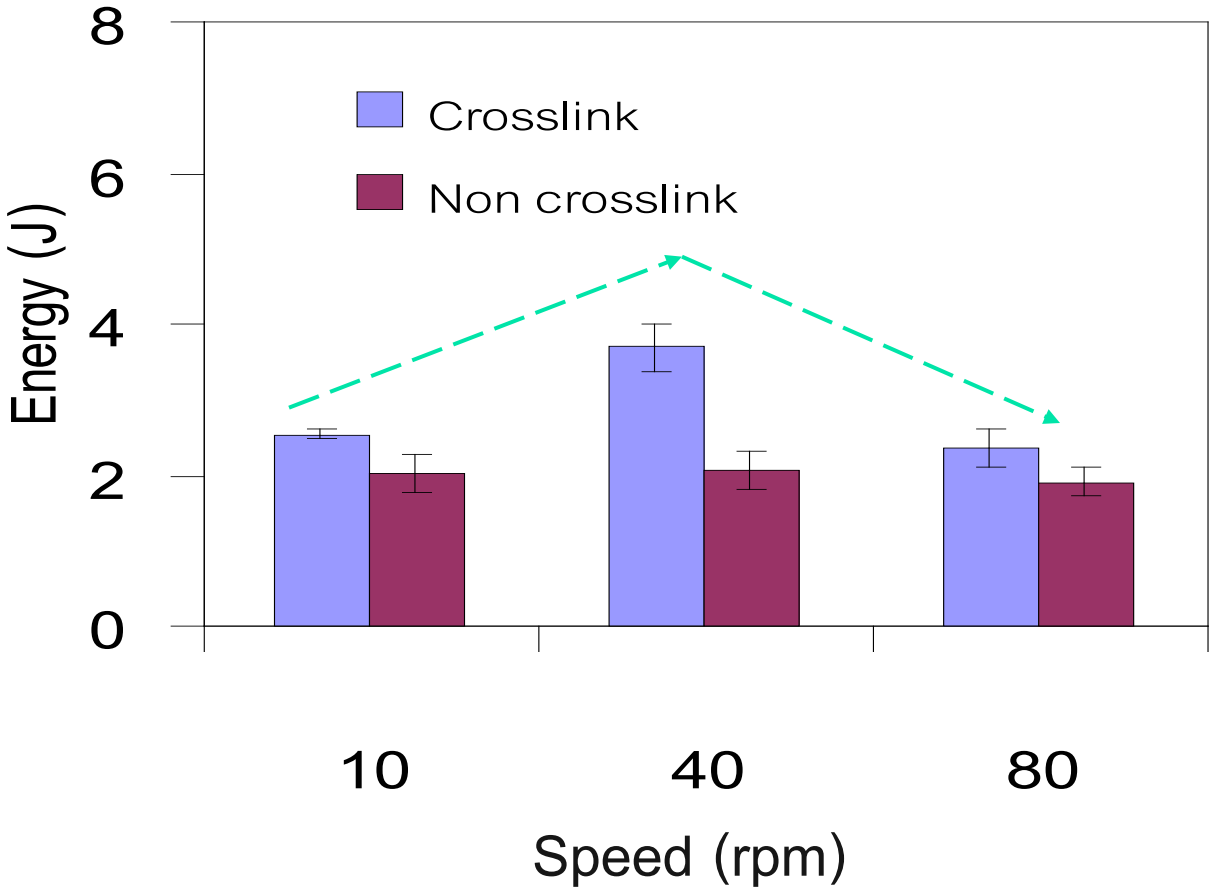
Effects of screw speed on tensile toughness of PVC/ACM (80/20) blends



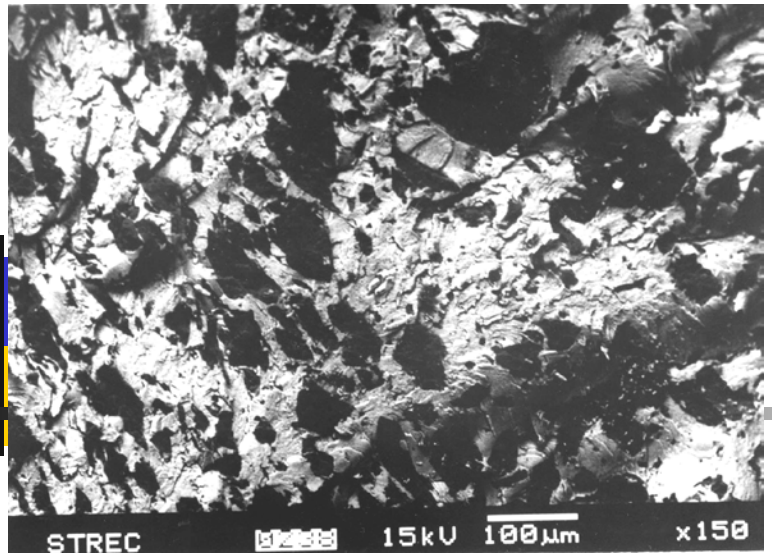
Effect of screw speed on toughness of PVC/ACM (70/30)



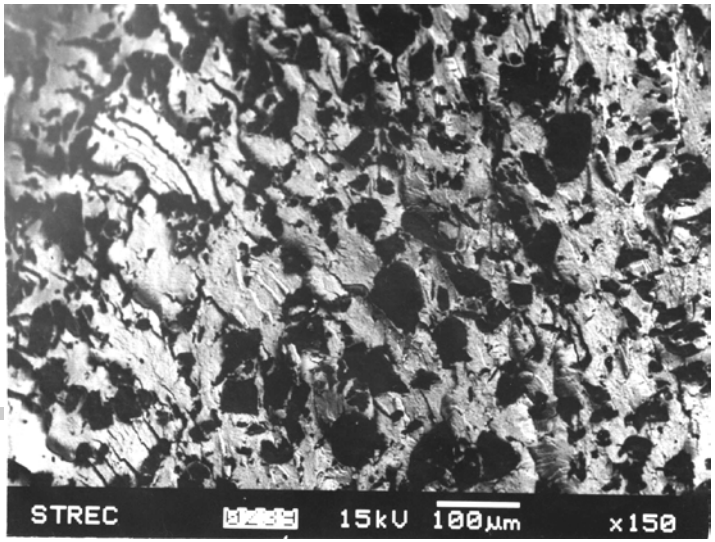
Effect of screw speed on toughness of PVC/ACM (60/40) blends



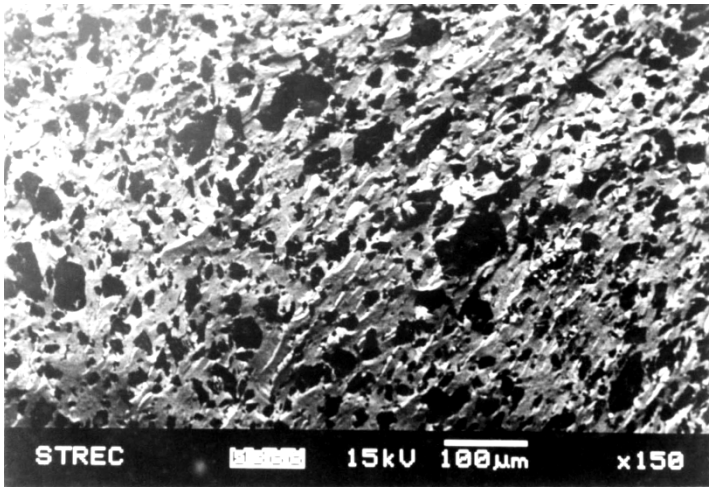
Effects of screw speed on morphology of NR/ACM (70/30) blends experienced dynamic vulcanization



10 rpm

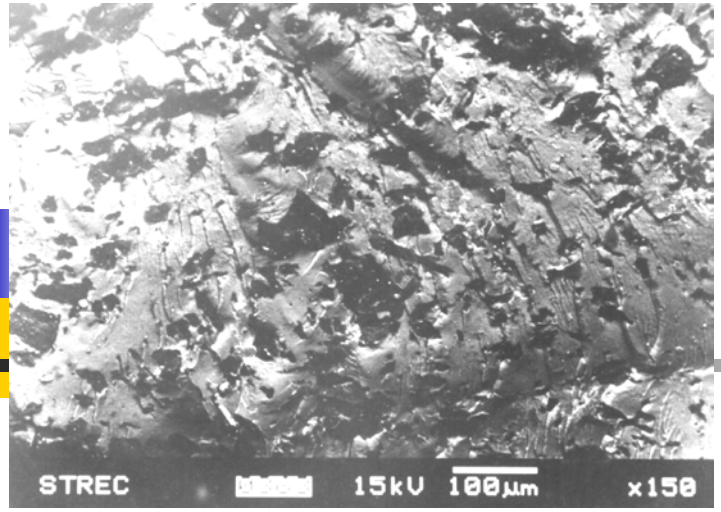


40 rpm

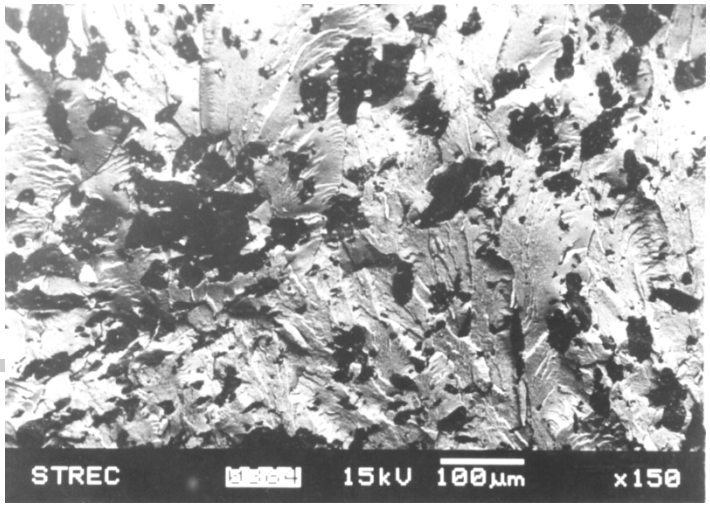


80 rpm

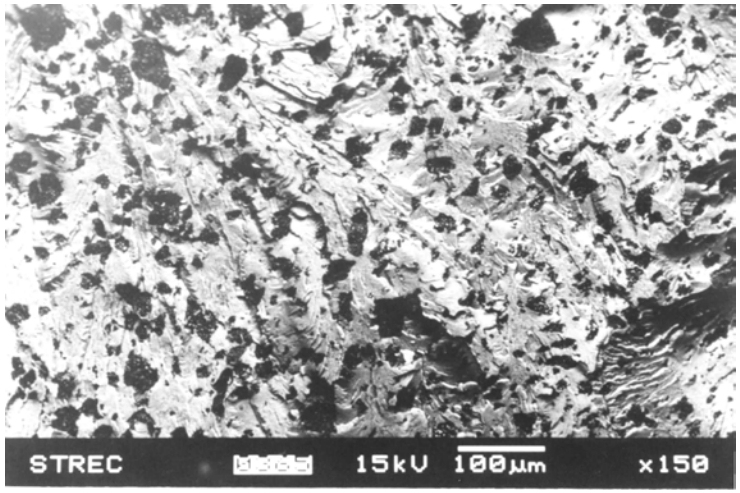
Effects of screw speed on morphology of NR/ACM (80/20) blends experienced dynamic vulcanization



10 rpm

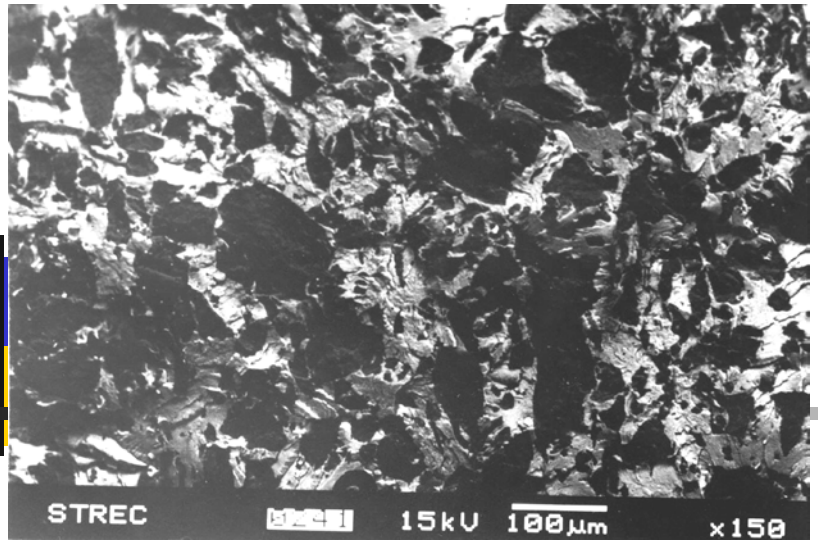


40 rpm

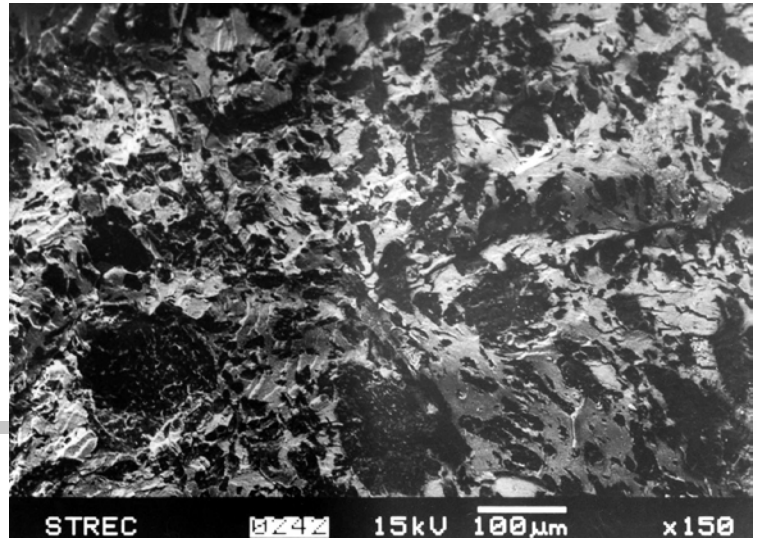


80 rpm

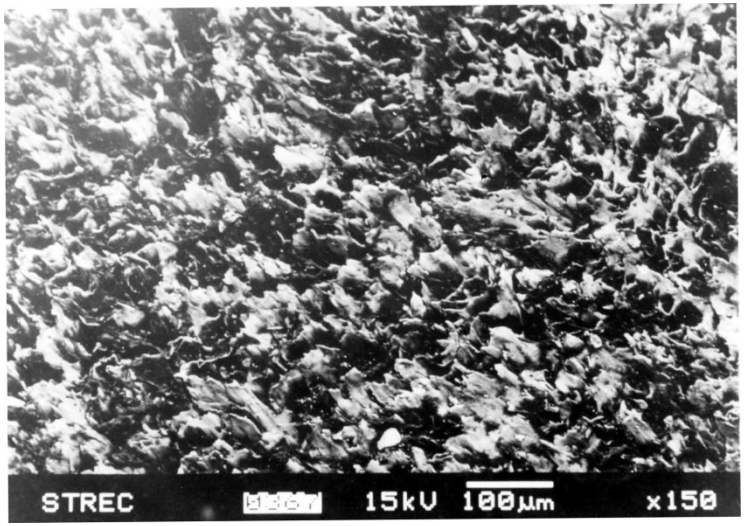
Effects of screw speed on morphology of NR/ACM (60/40) blends experienced dynamic vulcanization



10 rpm

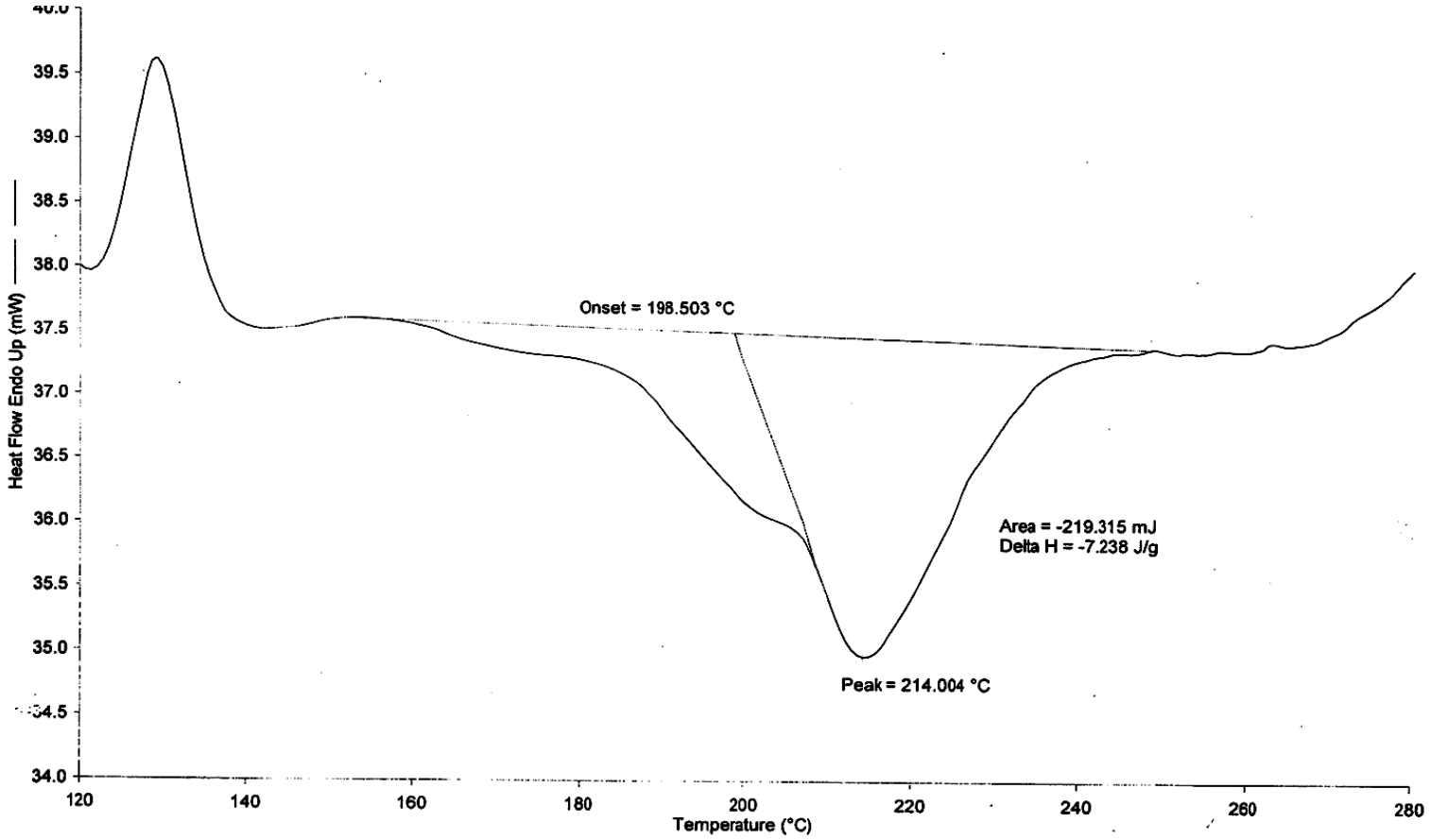


40 rpm



80 rpm

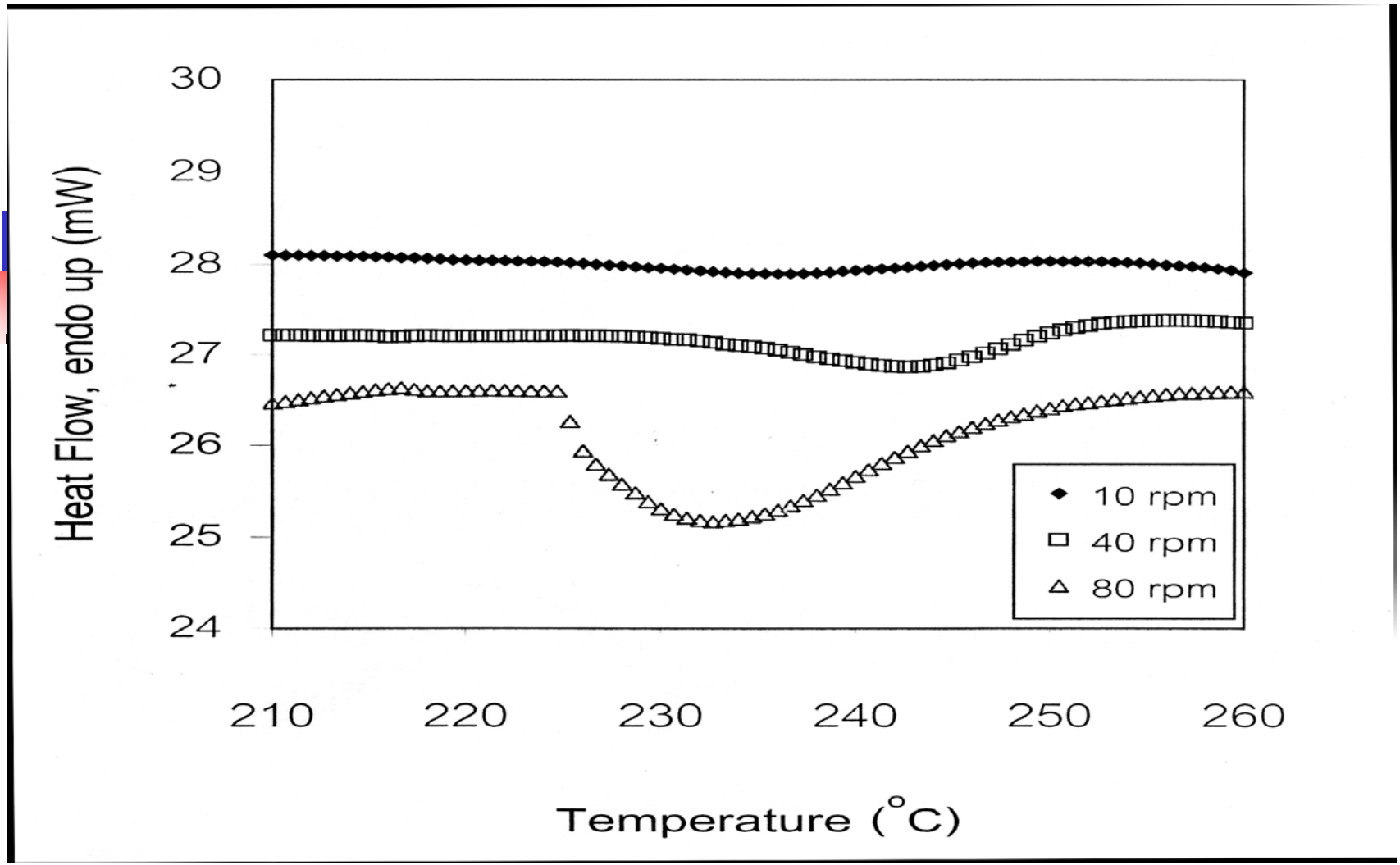
DSC Thermogram AR (ACM) compounded with sulfur (1 phr) and soap (10 phr)



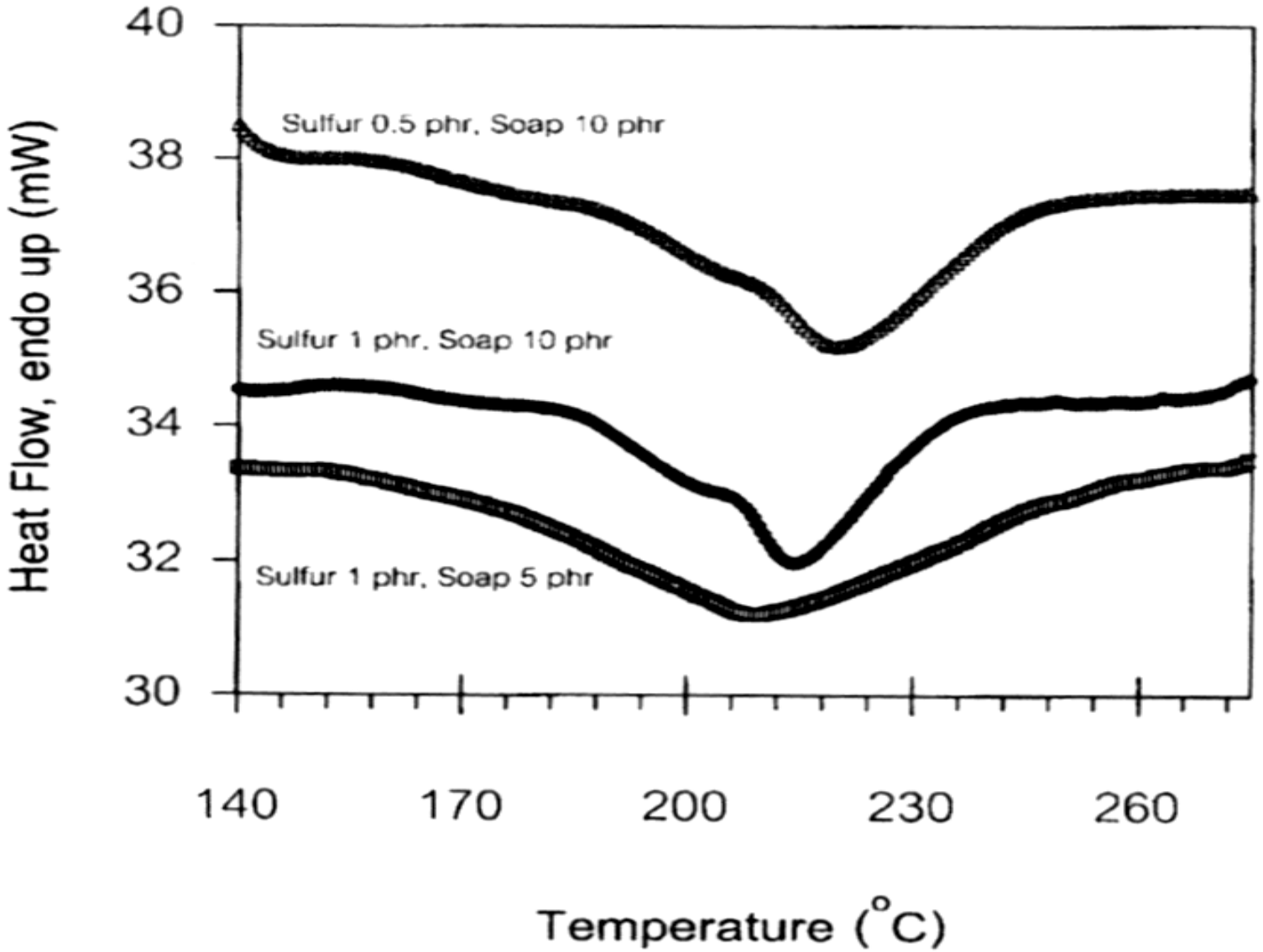
Enthalpy (J/g_{ACM}) of PVC/ACM (60/40) blends

ACM weight content (%)	Screw speed (rpm)	Enthalpy (J/g)
40	10	0.5
	40	1.4
	80	5.6
30	10	2.3
	40	3.0
	80	4.8
20	10	5.0
	40	9.9
	80	12.3

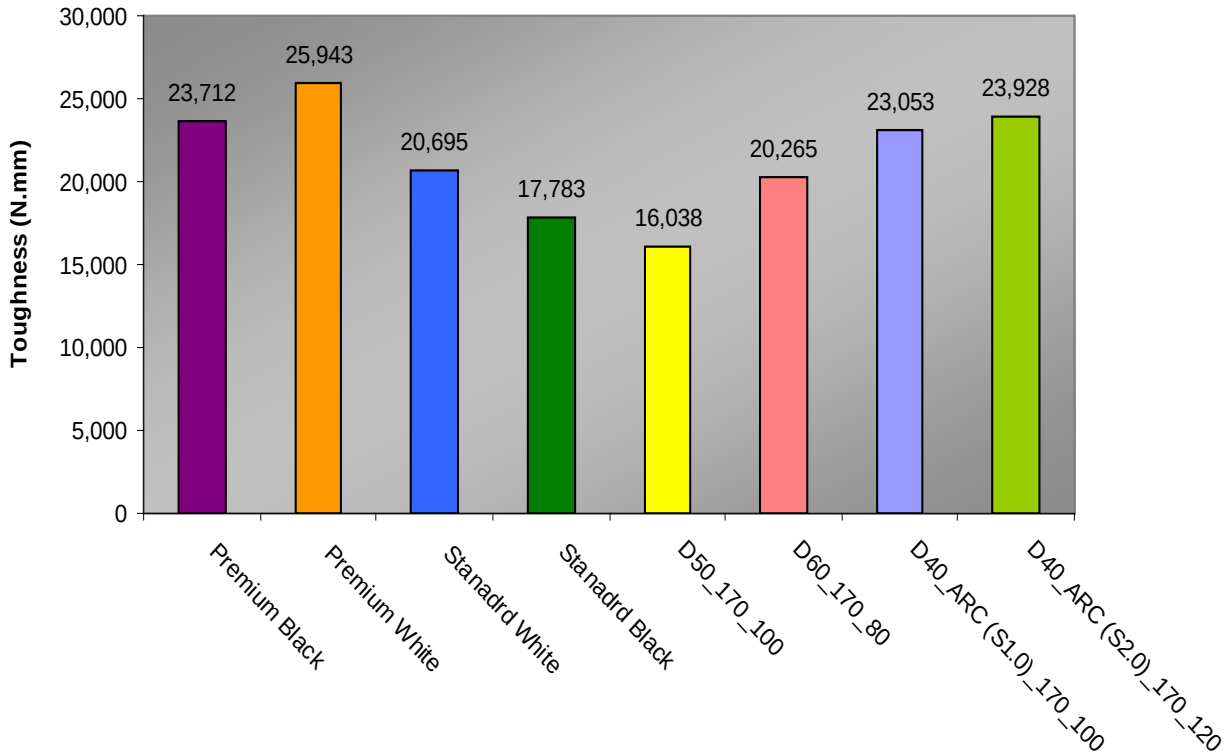
DSC thermogram of dynamically vulcanized PVC/ACM (60/40) blends



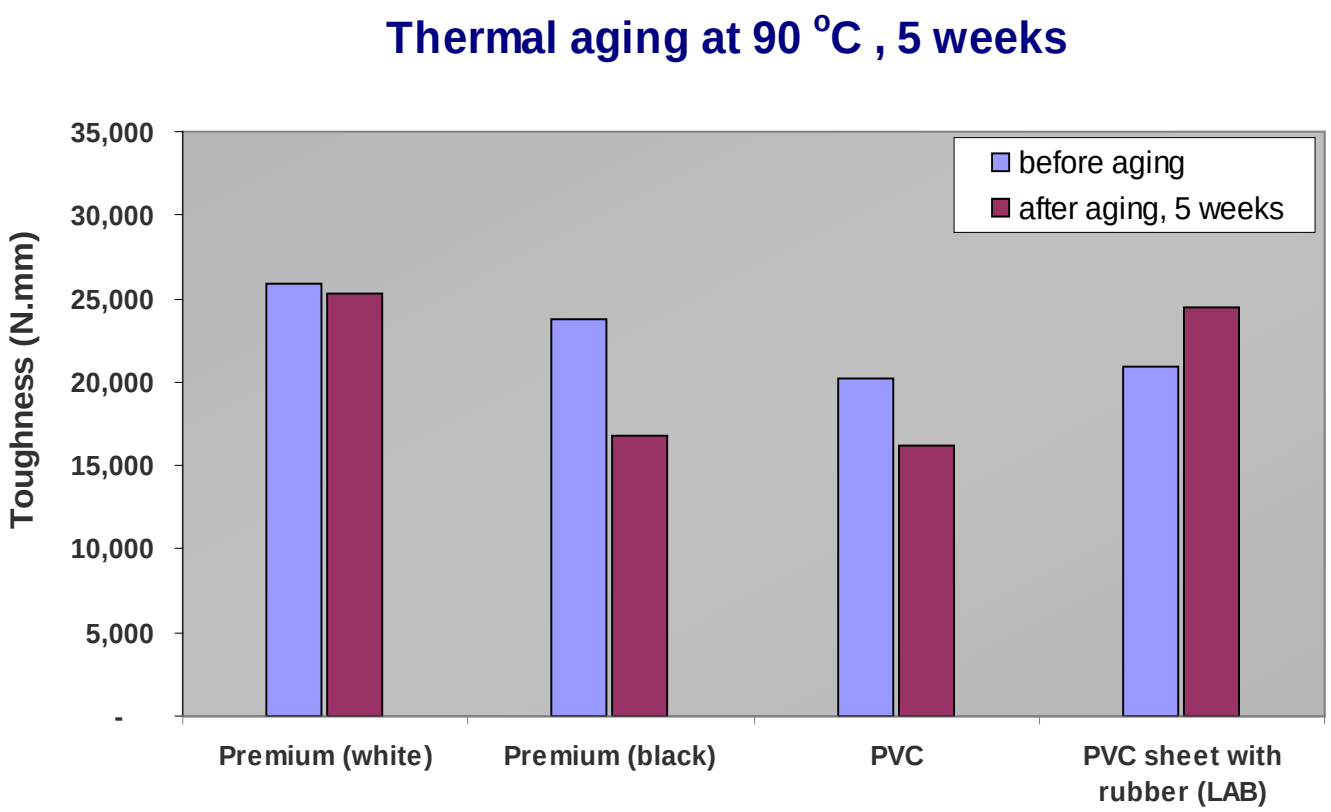
DSC thermograms of ACM compounds with different sulfur and soap content



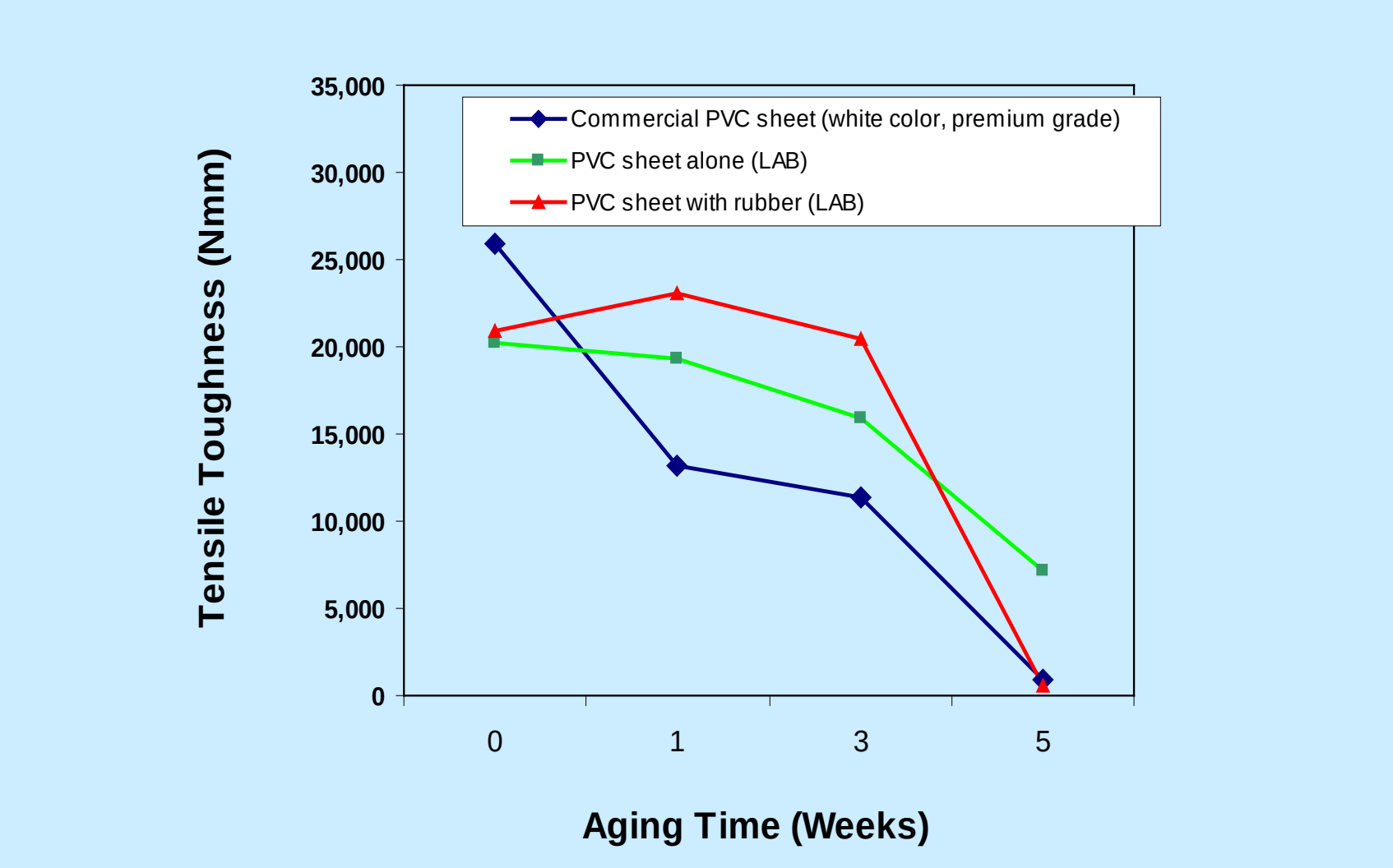
Tensile toughness of various PVC sheets



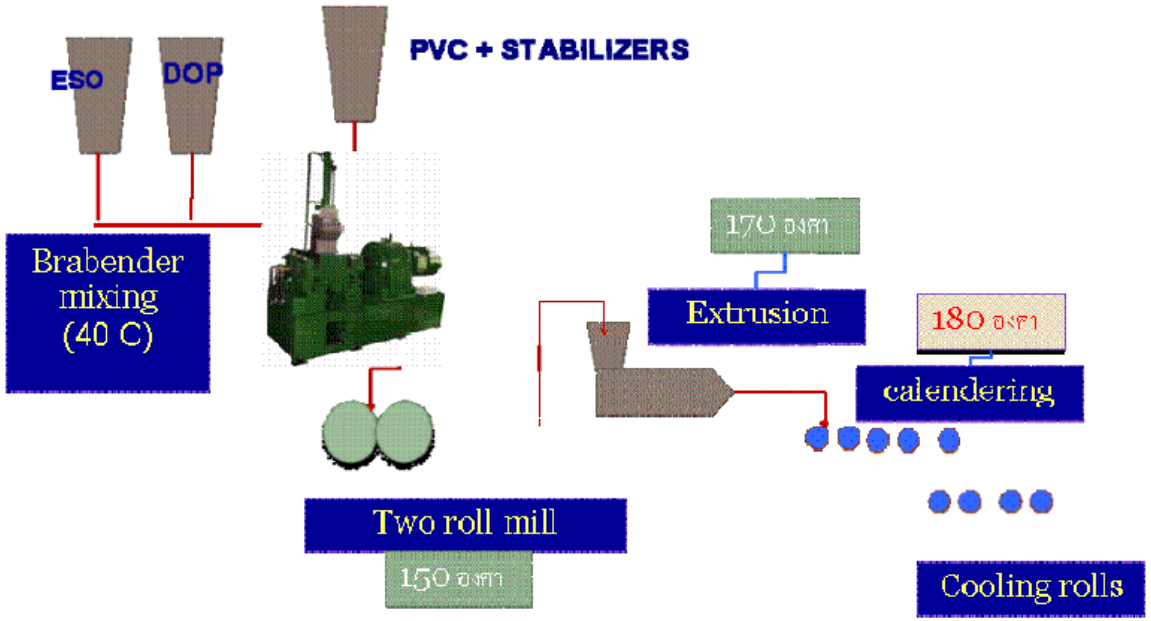
Tensile toughness after thermal aging



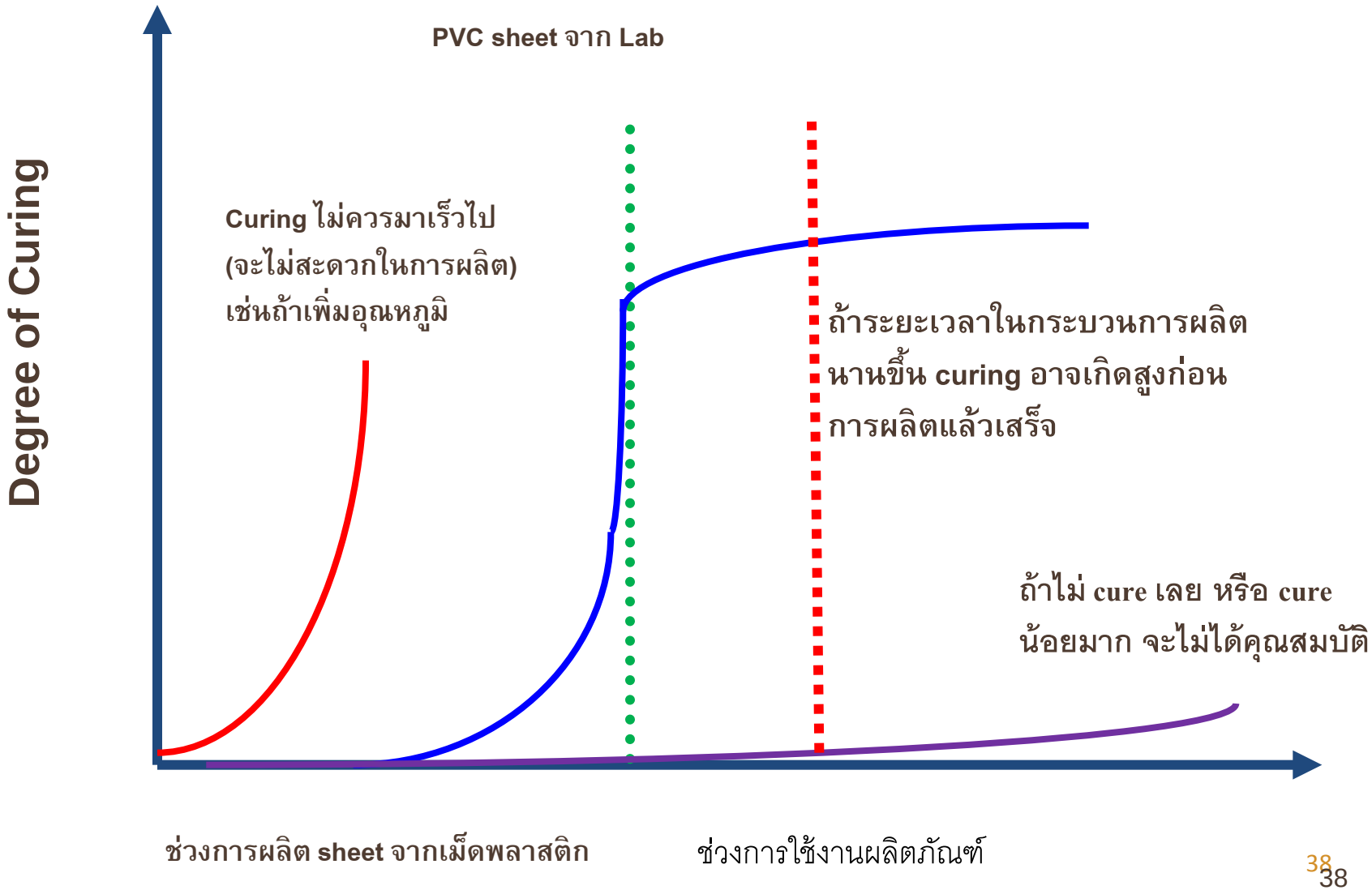
Change in toughness with aging time (at 155 °C)



กระบวนการผลิตแผ่นชีทพีวีซีในโรงงาน



แนวคิด ในการควบคุมอัตราการเกิดปฏิกิริยา Curing ของเฟสยาง ในระหว่างผสมและผลิต



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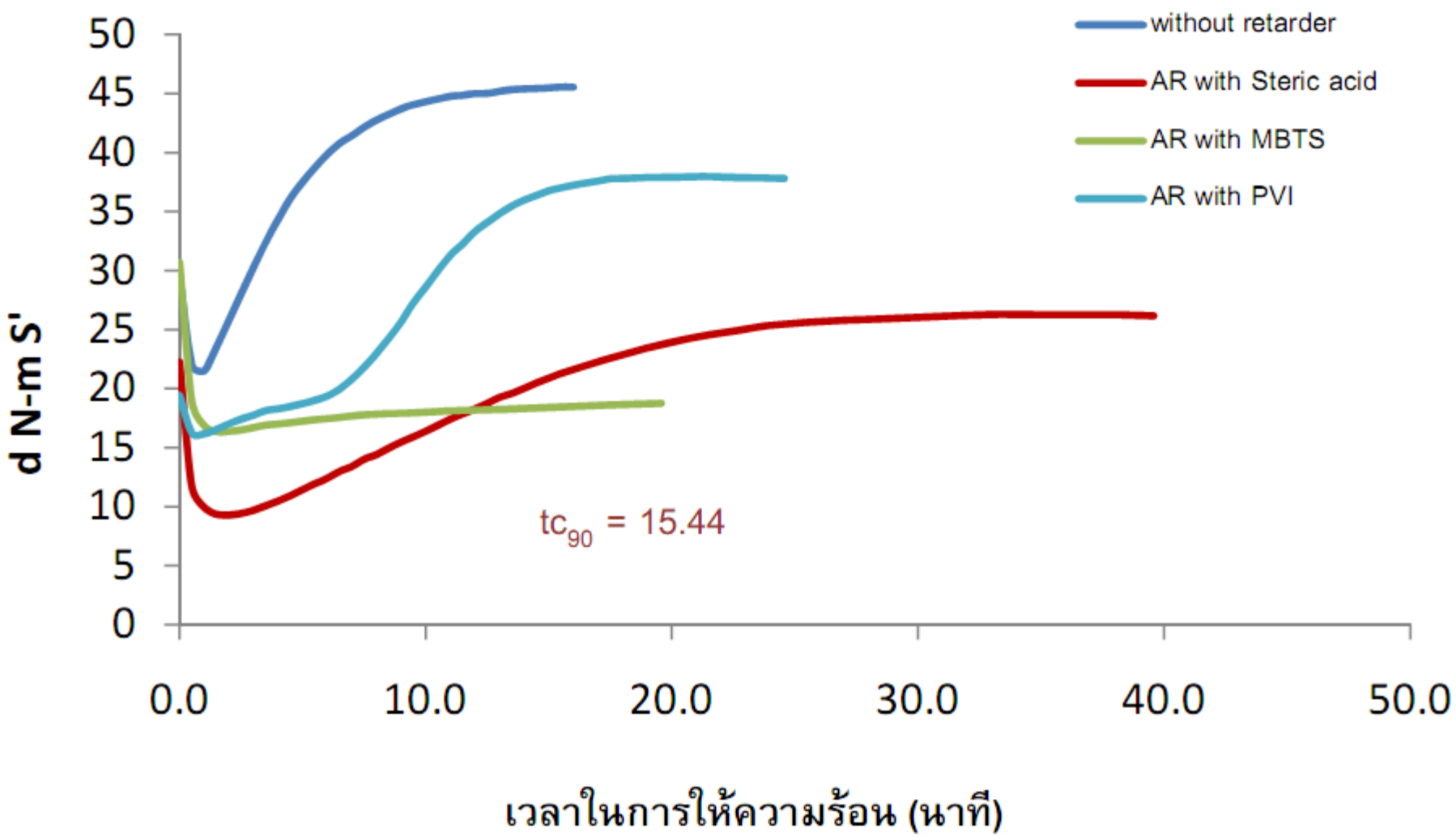
กราฟ ODR ของยางอะคริลิคคอมปาวด์ที่ผสมสาร retarder ชนิดต่าง ๆ



ค่าเวลาในการคงรูป(t_{90} และ t_{100})ของยางอะคริลิคคอมปาวด์ชนิดต่างๆ

ประเภทของสารประกอบโลหะสเตียเรต	ชนิดของสารหน่วง (retarder)	เวลาในการคงรูปยางคอมปาวด์ (นาที)	
		t_{90}	t_{100}
Potassium stearate	-	2.56	10.00
Sodium Stearate	-	8.11	15.51
Sodium Stearate	MBTS (3 phr)	15.44	18.50
Sodium Stearate	PVI (1 phr)	13.58	21.03
Sodium Stearate	Steric acid (3 phr)	21.54	32.44

Cure time ที่ 170 °C ของ acrylic rubber ที่เติม Steric acid ในปริมาณต่าง ๆ

Steric acid content (phr)	Cure time at 170 °C (min)	
	t_{90}	t_{100}
0.5	8.49	14.32
1.0	12.19	22.19
3.0	18.54	33.33
5.0	19.23	29.02
7.0	24.03	37.11

Steric acid (phr)	Cure time at 180 °C (min)	
	t_{90}	t_{100}
0.5	5.09	8.11
1.0	6.15	10.28
3.0	9.15	14.13
5.0	9.51	14.34
7.0	12.18	17.57

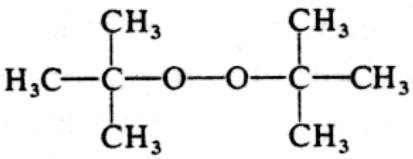
Curing agents

Peroxides

- Normally used for saturated molecules (EPR, EVA)
- Can also be used as an initiator for polymerization
- Can also be used to induce grafting and chain branching (e.g. PP-g-MA)
- Peroxide is unstable, can be explosive, depending on half-life and storage conditions

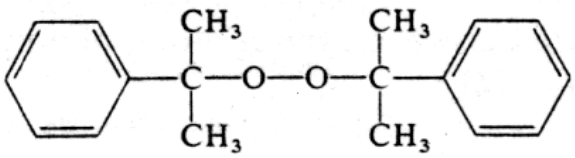
Examples of alkylperoxides

Dialkyl peroxides, e.g. di-tert.-butyl peroxide:



Physical form at 23 °C: liquid,
decomposition range:
approx. 190 °C,
usage: e.g. direct addition
to cable insulation and
sheathing compounds.

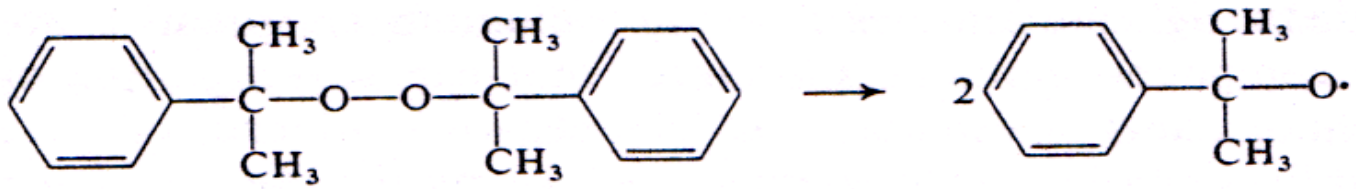
Diaralkyl peroxides, e.g. dicumyl peroxide:



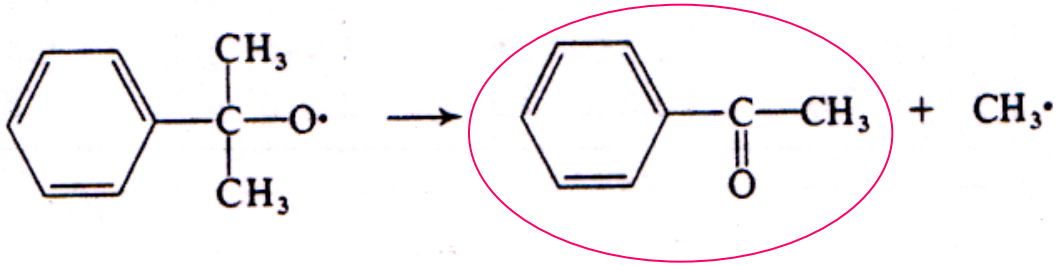
Physical form at 23 °C:
crystalline,
decomposition range:
approx. 170 °C,
usage: wide range of
applications.

(from Plastic Additives Handbook, edited by R. Gachter and H. Muller)

Mechanism of radical reactions from decomposition of DCP



The cumyloxy radical can also lead to the formation of a methyl radical and of acetophenone, a substance with an **unpleasant odor**



(from Plastic Additives Handbook, edited by R. Gachter and H. Muller)

Advantages and disadvantages of using curing with peroxide

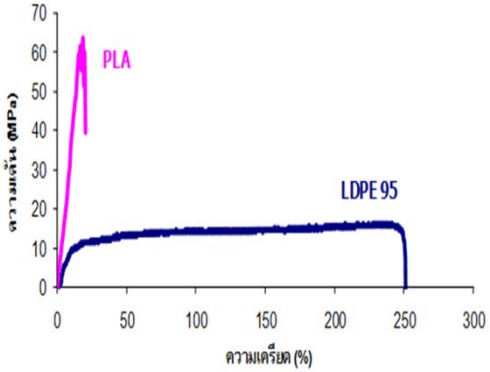
Advantages	Disadvantages
Low tension set	Low mechanical properties
Simple compounding	Expensive cross-linking agent
No mould contamination	Cross-linking might be inhibited by some antioxidant
Good heat aging resistance	Long cure time
Transparent rubber is possible	

Case study

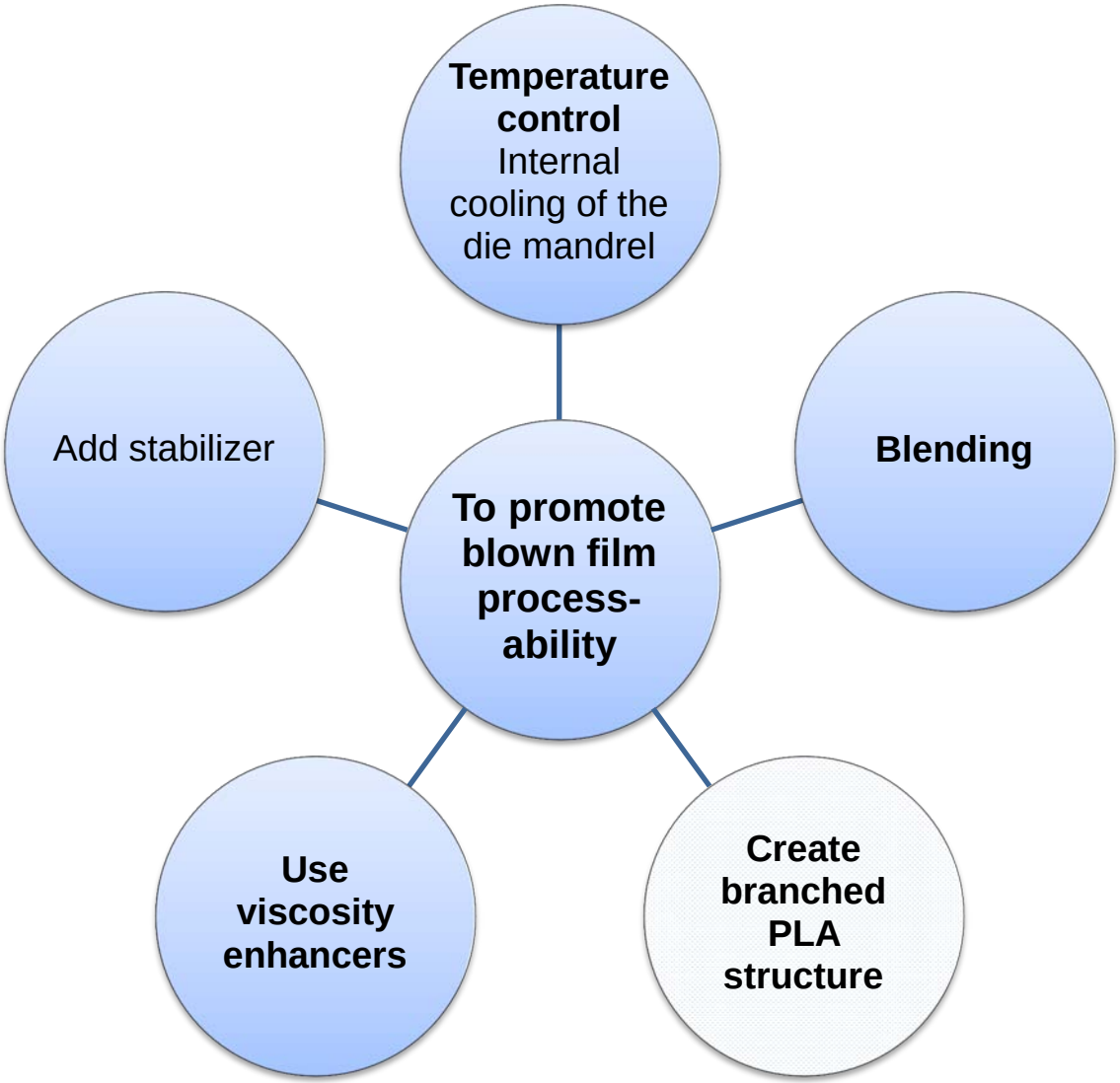
Compounding of PLA for preparing packaging film from extrusion blown molding

Problems related to blown film process-ability of PLA

1. PLA is brittle
2. Melt strength of the PLA is inherently low
3. Cost of the PLA is relatively high
4. PLA is thermally unstable, it can be degraded during the processing due to;
   - Hydrolysis
   - Chain scission



Some strategies for enhancing RHEOLOGICAL properties of the PLA during blown film process



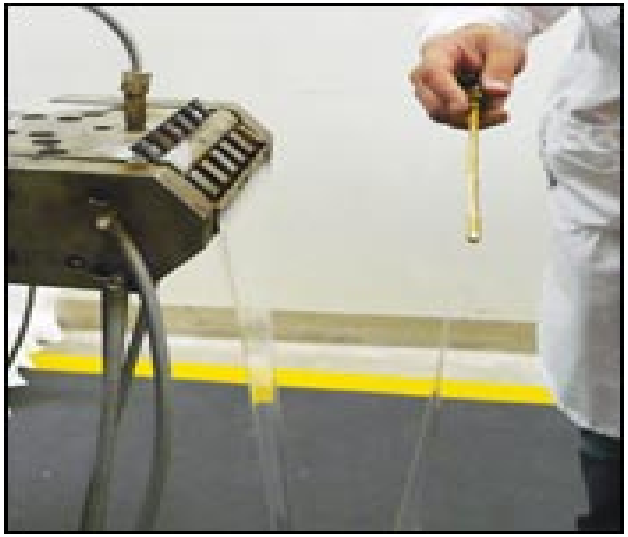
Viscosity enhancers

- To reverse the degradation by chemically coupling individual polymer strands
- Examples of the chemical include
  - CESA® (copolymer of styrene, MMA, GMA) [*US Patent 2007/0003774 A1 (2007)*]
  - Chain extenders such as isocyanates, oxazolines, dihydrooxazines, anhydrides [*US Patent No. 5,594,095*]

PLA film with (left) and without (right) Cesa-Extend from Clariant Masterbatches.

(Reference: Plastic Additives & Compounding, May/June, 2008, p.24)

Biostrength 700



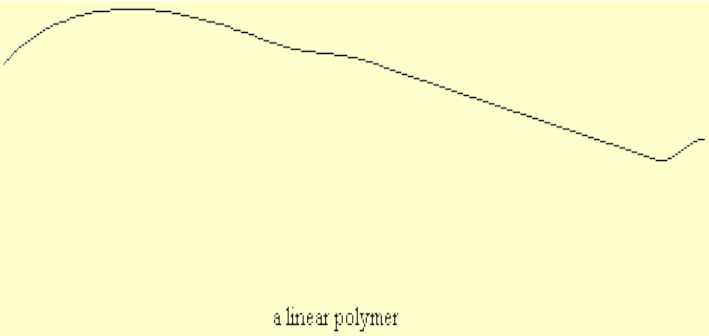
Arkema's Biostrength 700 **acrylic copolymer** has been shown to double the melt strength of PLA at 4% addition level (right) vs. a neat PLA (left).

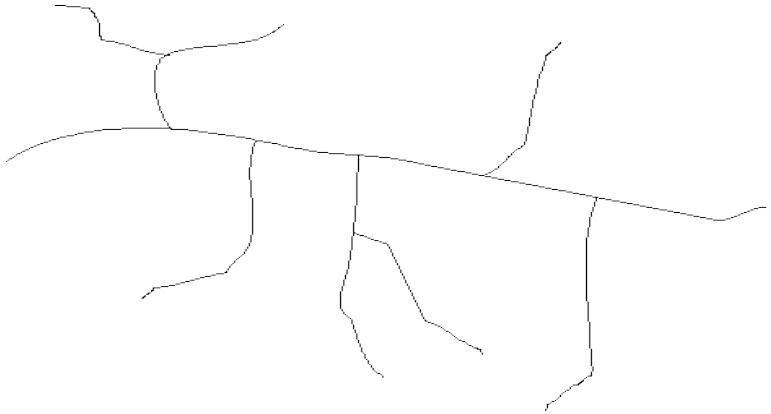
http://www.ptonline.com/articles/200807fa1.html

How to induce branching of the PLA chains

- *By adding some peroxide compounds*

- By carrying out a reactive blending with other functional polymers
  - Epoxy functional acrylate polymer [*US patent 2008/0050603*]





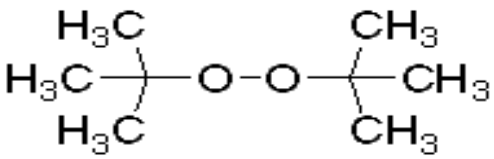
a branched polymer

สารเปอร์ออกไซด์ที่น่าสนใจ

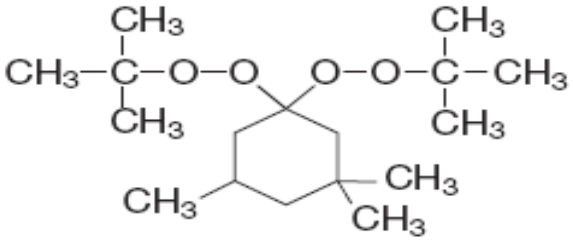
Recommended peroxides for this research work

Peroxides	Tradename	Half-life	Reasons/Advantages	Related References
2,5-dimethyl-2,5-di(tert-butylperoxy)hexane	Trigonox 101, Luperox101	~ 1 min @ 185 ºC	Capability of the chemical for improving **MFI** of PLA has been reported	Paul Lacobucci [Akzo Nobel Polymer Chemical]
Di-t-butyl peroxide	Luperox DI	1 min @ 193 ºC	FDA approved (**food grade**)	http://chemicalland21.com/specialtychem/perchem/DI-tert-BUTYL%20PEROXIDE.htm
t-butylperoxybenzoate	Trigonox C		Capability of the chemicals for improving **melt strength** of PLA has been claimed	L.T.Lim *et al*., Progress in Polym Sci., 33(2008)820-852
Dibenzoyl peroxide				A.Sodergard et al., US patent 6,559,244B2 (2003)
T-butylperoxy acetate	Trigonox F			

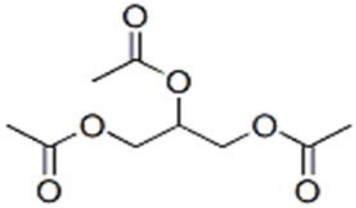
Peroxides and plasticizers for PLA



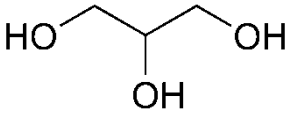
Luperox DI



Luperox 231

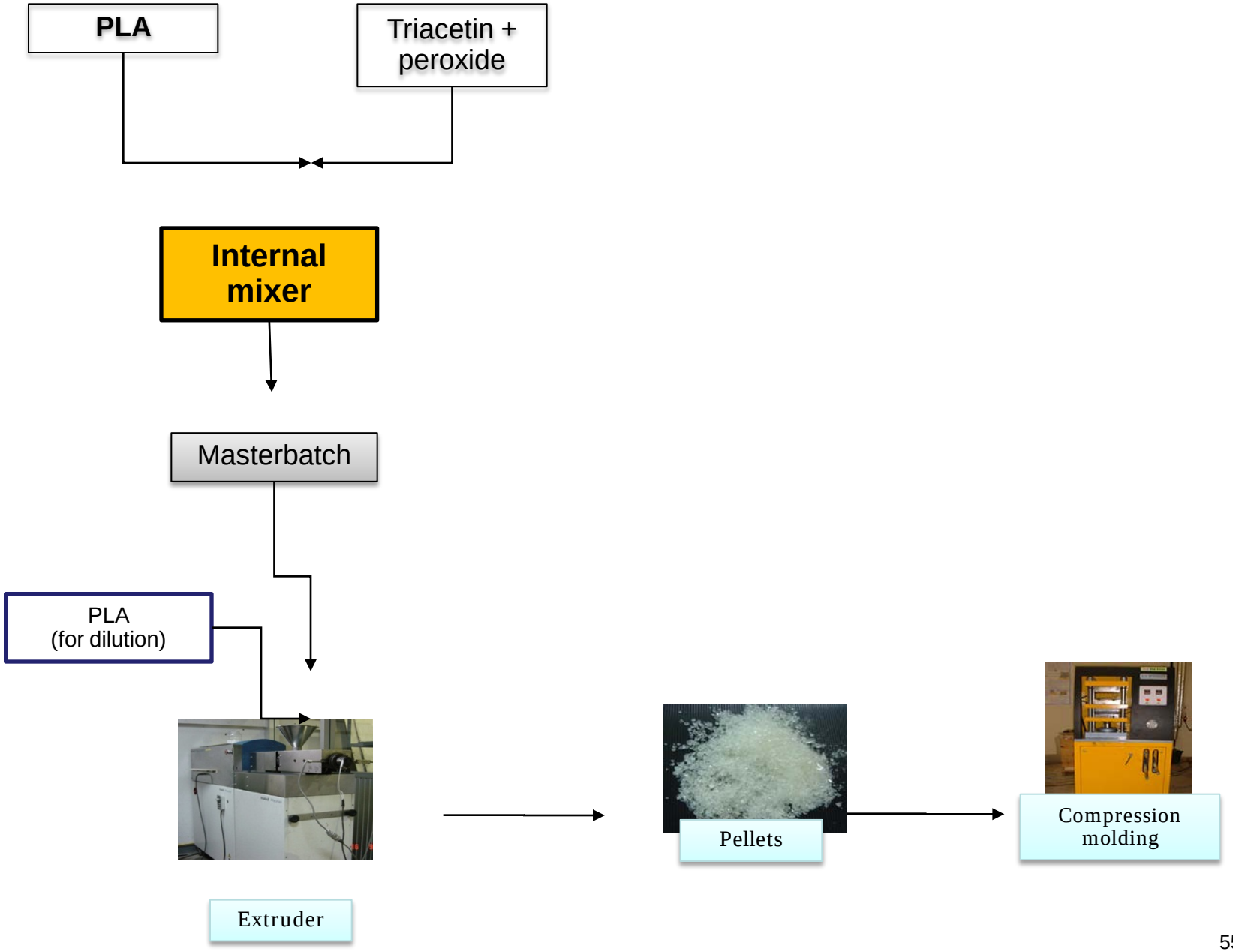


Triacetin



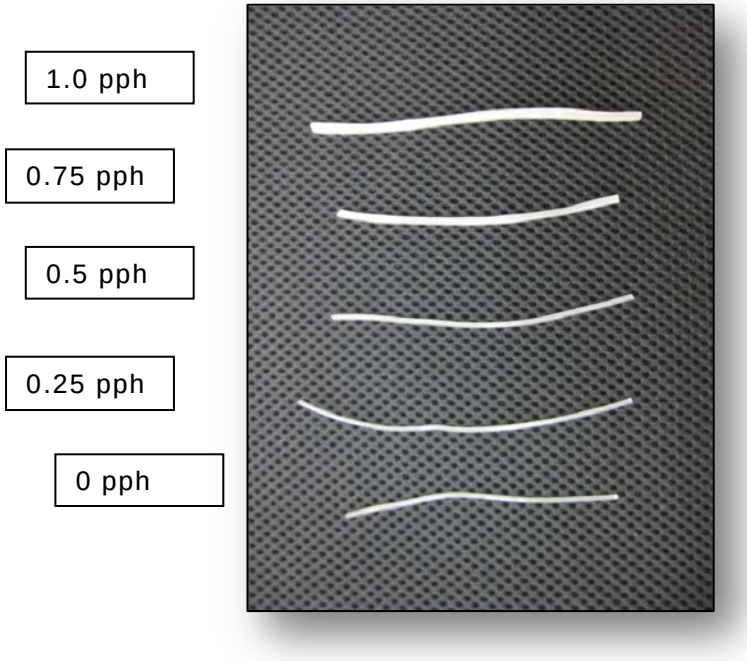
Glycerol

การผสมแบบเตรียมผ่าน masterbatch



Effect of peroxide (Luperox 231) content on gel content

ปริมาณสาร Luperox 231 (pph)	ปริมาณเจล (%) (ในตัวทำละลายไดคลอโรมีเทน)
0	0
0.50	0
0.75	0
1.00	0



ลักษณะของฟิล์ม PLA (ผสม triacetin 20 pph และใช้ Luperox 231 ในปริมาณ 0.75 pph) ระหว่างการเป่าขึ้นรูป

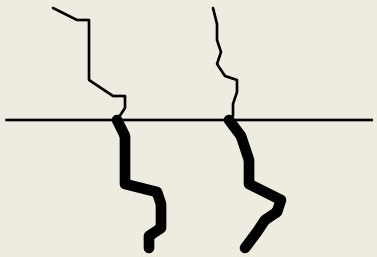
แนวทางการแก้ปัญหาเรื่องการเหนียวติดของฟิล์ม

1. ลดปริมาณ triacetin (สารเปอร์ออกไซด์คงที่ 0.75 pph)
2. เติมสาร anti-blocking เช่น talc, calcium carbonate, TiO_2, SiO_2 หรือแม้แต่ starch ในกรณี PLA/starch blend

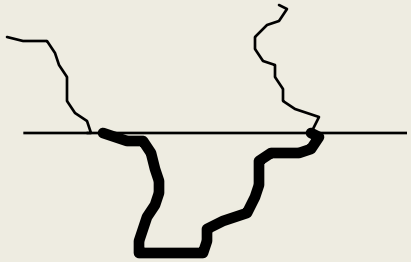
Compatibilizers

Orientation of copolymers at interfaces

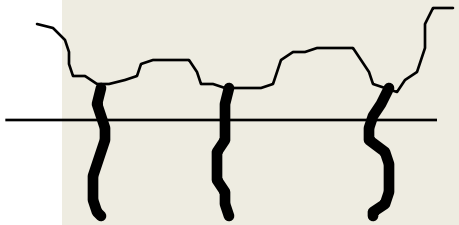
- Di-block copolymer



- Tri-block copolymer

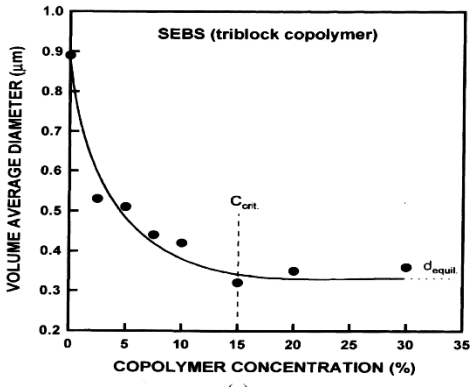


- Graft copolymer

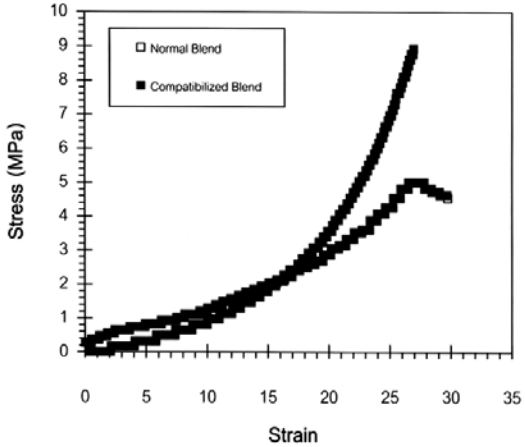


Primary roles of block copolymers

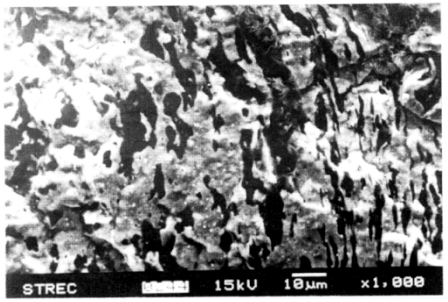
- To reduce the interfacial tension between phases
- To prevent coalescence between minor phase particle
- To improve the adhesion between phases



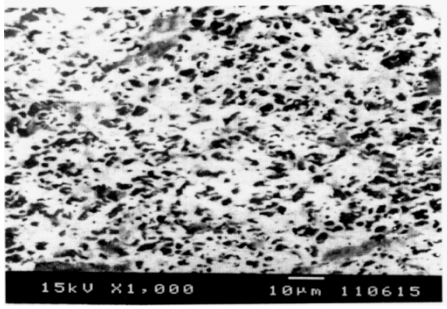
Effects of PI-PBA block copolymer on mechanical properties of NR/ACM blends



Normal blend

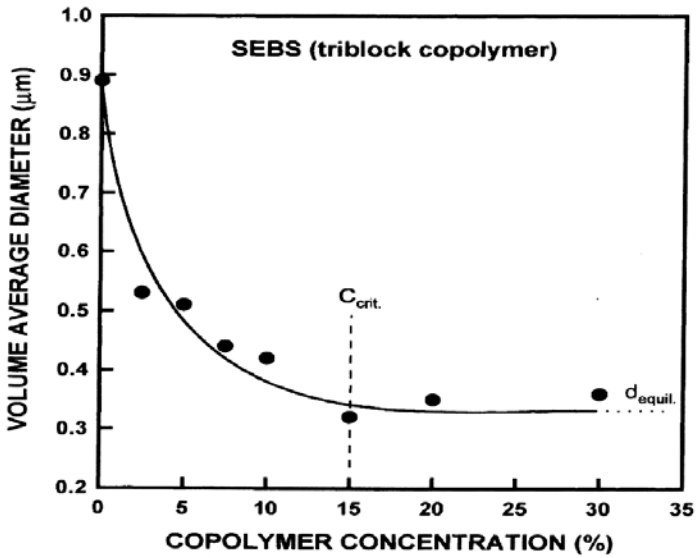


Compatibilized blend



Roles of copolymers on particle size

- **The reduction in particle size is related to**
  - **Decrease in an interfacial tension**
  - **Reduction of coalescence.**



- **In order to differentiate between the above 2 effects emulsification curves at low (1 % no coalescence) and high concentration of dispersed phase should be considered**

A-C type compatibilizers

Polymer A	Polymer B	Compatibilizer
PVC	PS	PCL-b-PS
PS	PE	PS-g-Polybutadiene, SIS, SBS, SEBS, hydrogenated SB
PS	PA	PS-g-PMAH,
PE	PA	Carboxylated PE (g)
PE	PVF_2	Hydrogenated Polybutadiene-g-PMMA
PP	PA	PP-g-PMAH, MAH grafed PP
PP	PET	Glycidyl methacrylate grafted PP
PS	EPDM	SEBS

C-D type compatibilizers

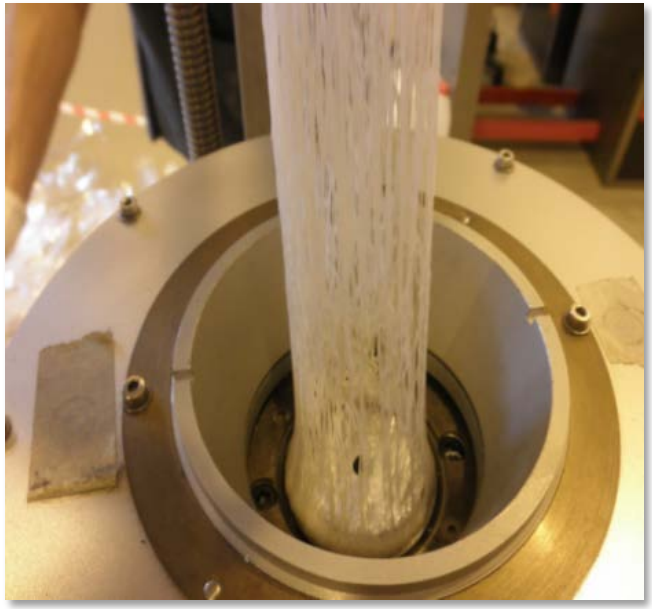
Polymer A	Polymer B	Compatibilizer
PVC	LDPE	PCL-b-hydrogenated polybutadiene
SAN	Poly(phenylene ether)	PMMA-b-PS
SAN	SBR	PMMA-b-Polybutadiene
PE	PET	Hydrogenated-SIS, -SEBS
PP	PMMA	SEBS
Poly(phenylene ether)	PVF_2	PS-b-PMMA

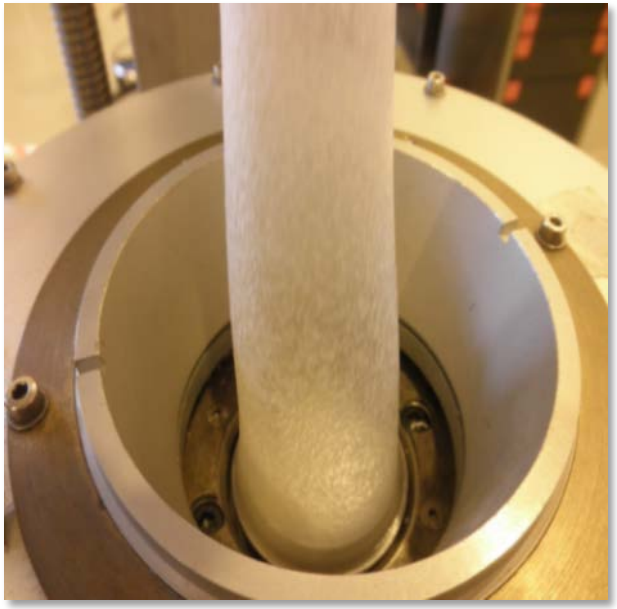
E- type compatibilizers

Polymer A	Polymer B	Compatibilizer
PVC	PS	Chlorinated PE
PS	PA	Styrene-r-MAH copolymer
PVC	Polybutadiene	Ethylene-r-vinyl acetate copolymer
PVC	Natural rubber	Epoxidized NR (a kind of random copolymer)
PP	PA	Ethylene-r-acrylic acid copolymer

Case study:
Compatibilization of PLA/thermoplastic starch blend

PLA/TPS blown film



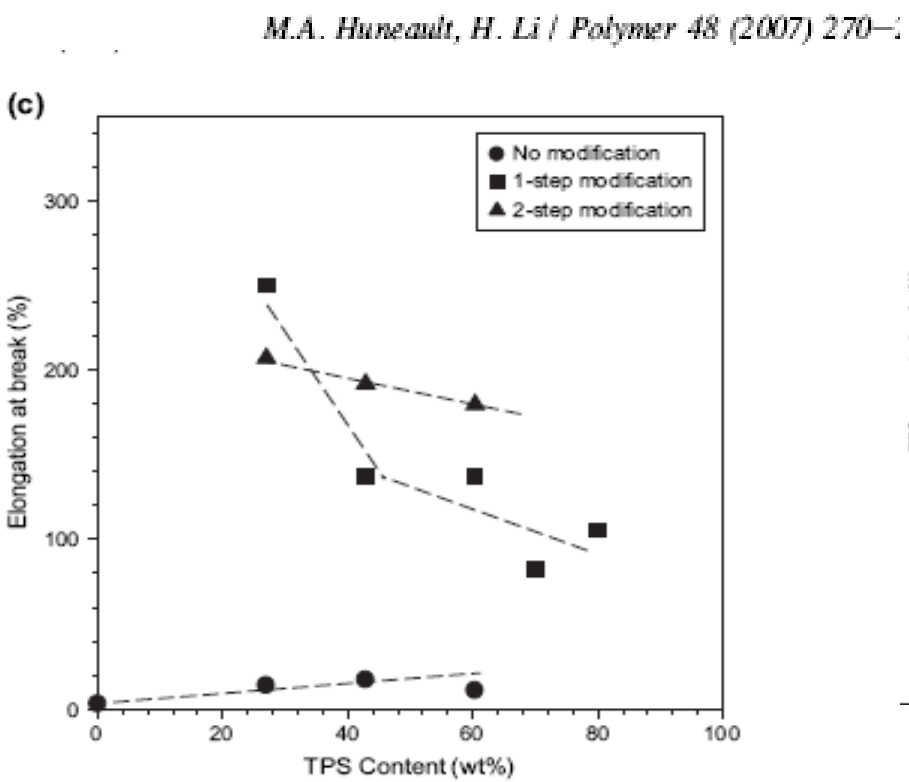


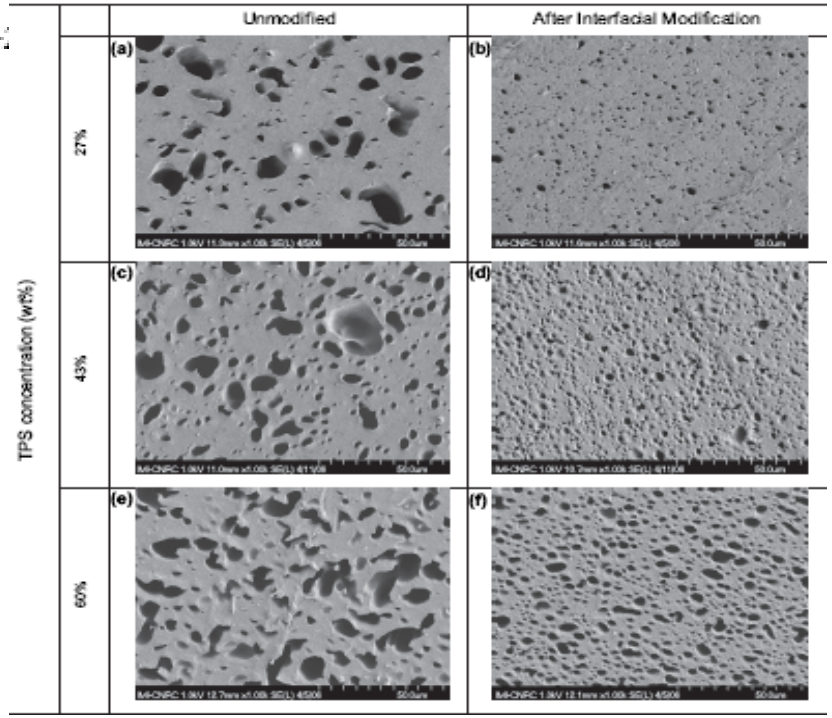
ลักษณะของลูกโป่ง *p*-PLA/TPS (สัดส่วนผสมร้อยละ 70/30 โดยน้ำหนัก) ขณะเป่าขึ้นรูป ที่อุณหภูมิ 170 องศาเซลเซียส (ภาพซ้าย) และ 135 องศาเซลเซียส (ภาพขวา)

The problem is partly attributed to poor compatibility between PLA and TPS

Some related work

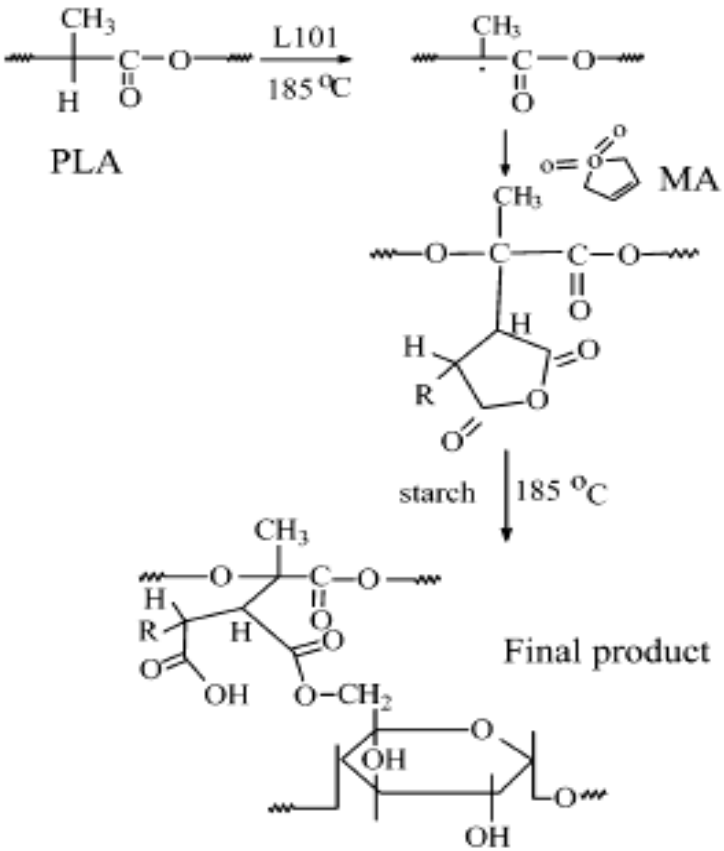
Work by Huneault et.al.,(Polymer, 2007) showed that with the use of more efficient compatibilizing technique, greater starch content can be loaded





Definitions:
One step process = the prepared PLA-g-MA was directly reacted with TPS
Two step process = the prepared PLA-g-MA was pelletized prior to blending with PLA and TPS

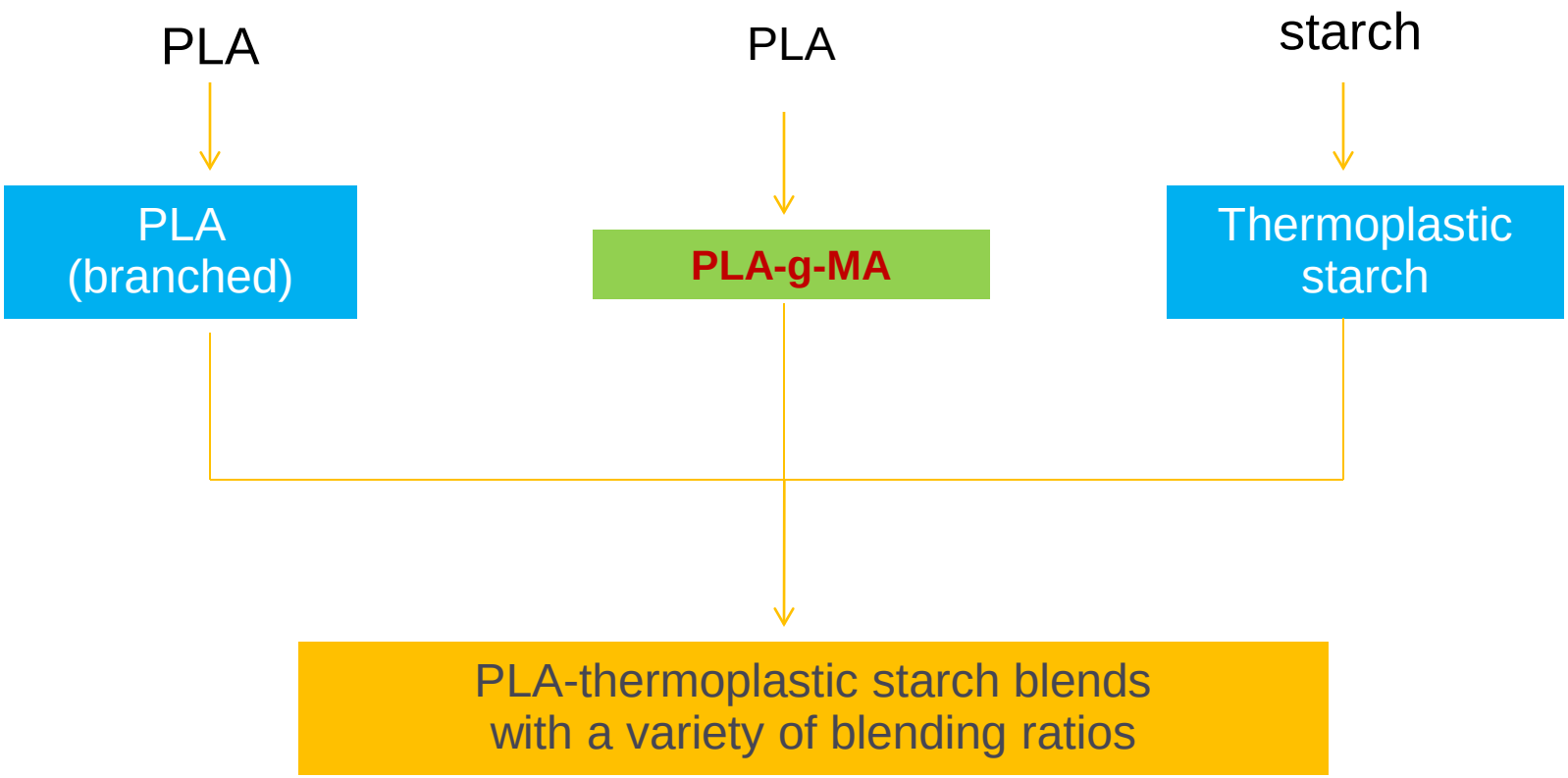
PLA-starch blends (one step process)



Biomacromolecules **2004,** *5, 1446−1451*

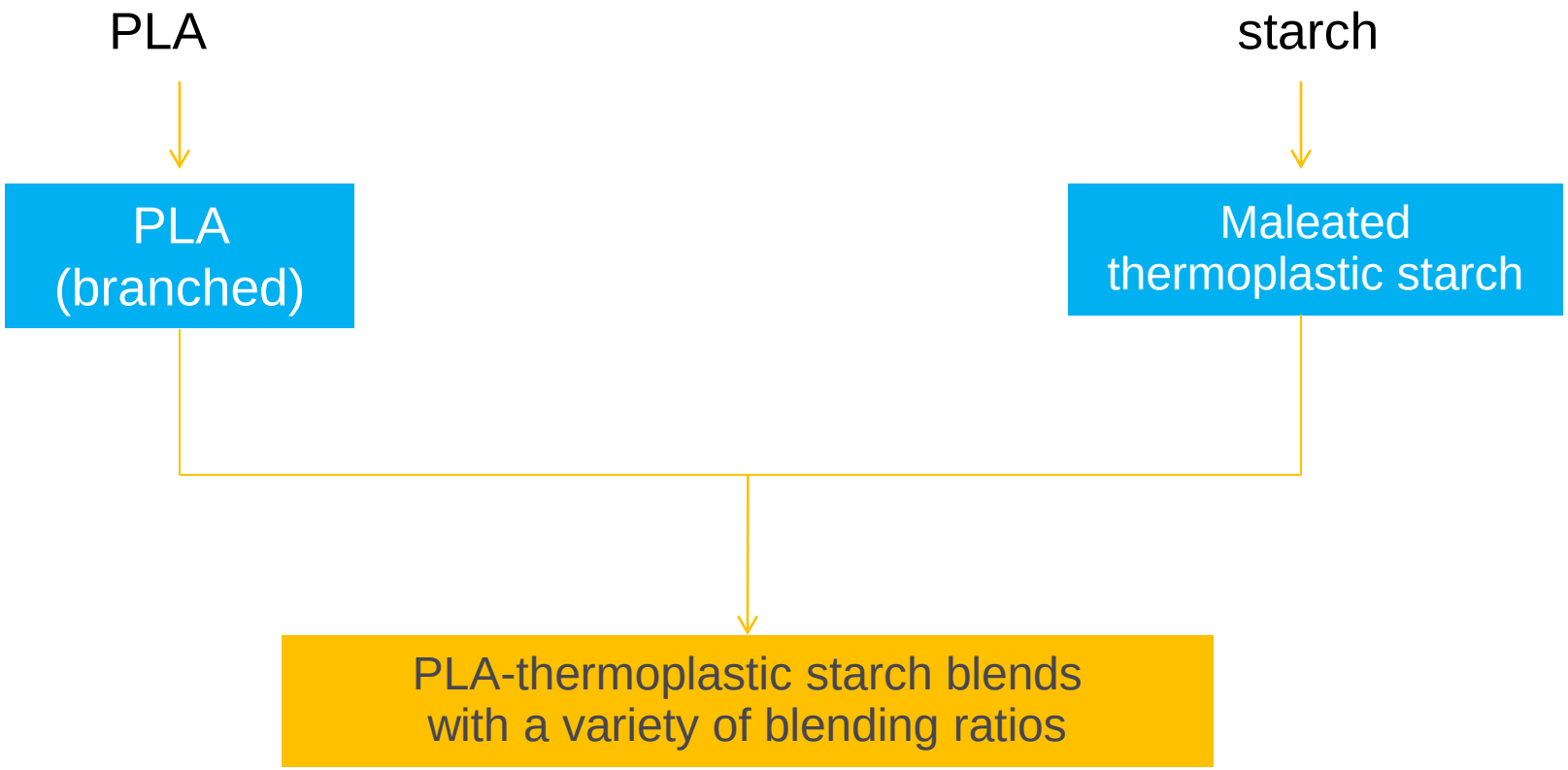
Compatibilization of PLA/TPS

Scheme 1 using PLA-g-MA compatibilizer)

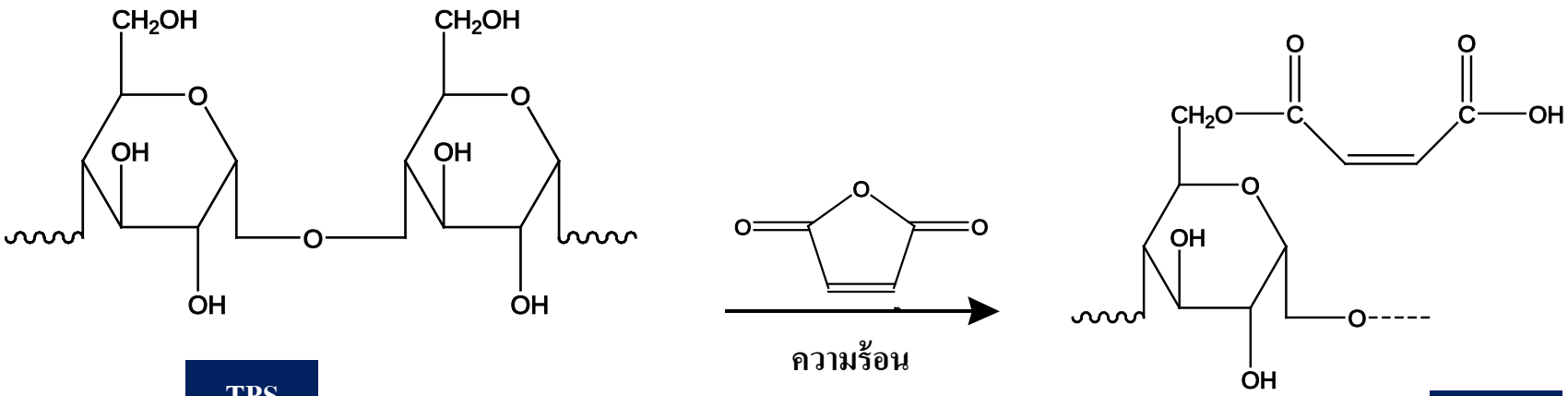


Scheme 2

Reactive blending of PLA-starch (trans-esterification)

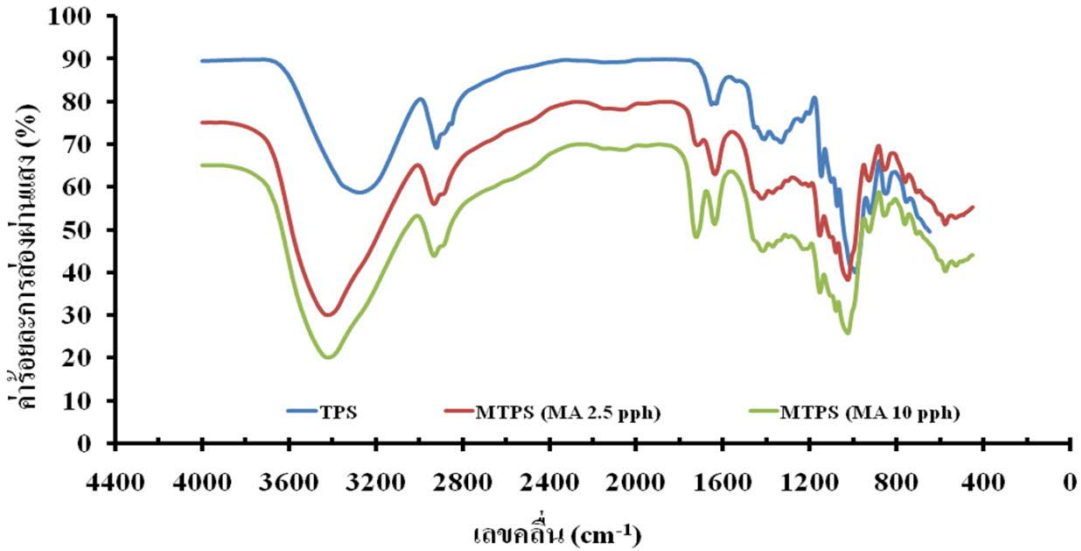


แป้งเทอร์โมพลาสติกมาลิเอต (MTPS)



TPS

MTPS



Tensile properties of PLA/MTPS blends

TABLE III
Tensile Properties of Various PLA/MTPS Blends (70/30% w/w), Prepared Under Various Time and Temperature

Blending conditions		Tensile properties			
Temperature (°C)	Time (min)	Tensile strength (MPa)	Elongation at break (%)	Modulus (MPa)	Tensile toughness (J)
170	7	9 (0.8)	377 (32)	135 (14)	2.3 (0.3)
170	12	8.7 (0.5)	212 (11)	92 (5)	1.2 (0.1)
180	12	13.8 (0.7)	149 (25)	113 (25)	0.6 (0.4)
190	12	13.0 (0.7)	79 (20)	141 (18)	0.5 (0.1)

TABLE IV
Melt Flow Index of Various PLA/MTPS (70/30% w/w) Blends

Time (min)	Temperature (°C)	Melt flow index (g/10 min)
7	170	23.3 ± 3.3
12	170	29.0 ± 5.1
12	180	44.7 ± 6.3
12	190	57.0 ± 6.2

TABLE V
Tensile Properties of PLA/TPS and PLA/MTPS Blends (70/30% w/w)

	Type of blends	
Tensile properties	PLA/TPS (70/30% w/w)	PLA/MTPS (70/30% w/w)
Tensile strength (MPa)	13.50 (± 0.80)	9.0 (± 0.78)
Elongation (%)	8.7 (± 0.34)	376.9 (± 31.86)
Modulus (MPa)	296.24 (± 20.90)	134.9 (± 13.77)
Tensile toughness (J)	0.06 (± 0.01)	2.3 (± 0.29)

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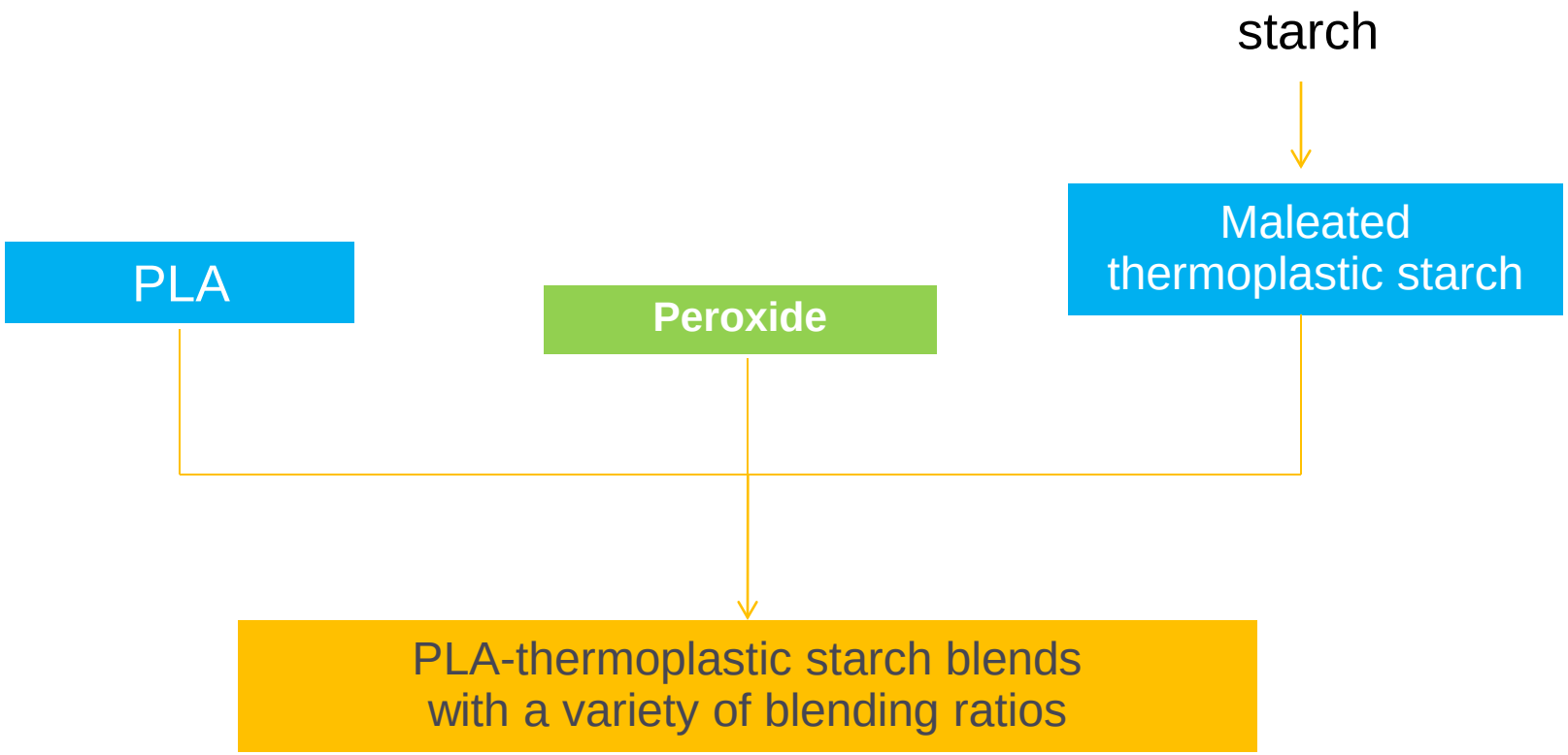
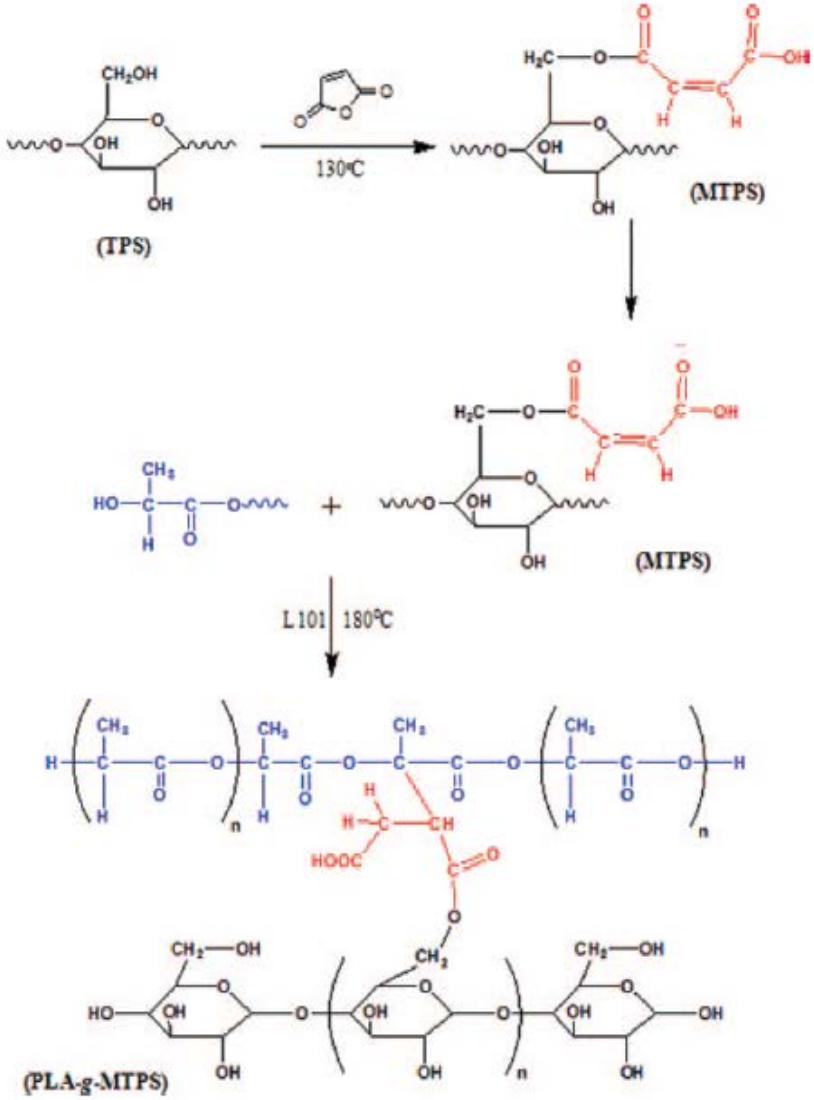
Scheme 3 ：Preparation of PLA-g-MTPS compatibilizer

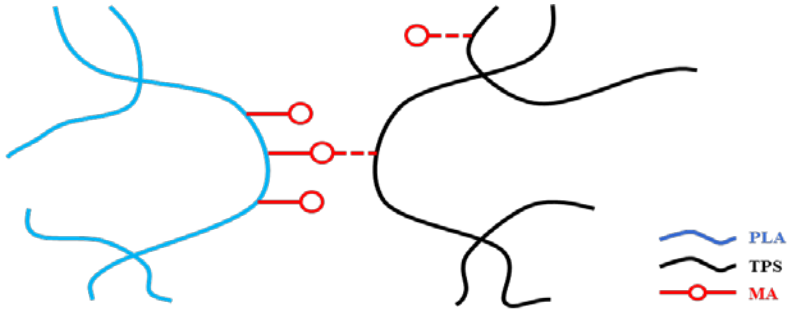


การเตรียม และโครงสร้างทางเคมีของ PLA-g-MTPS ที่คาดว่าจะเกิดขึ้น

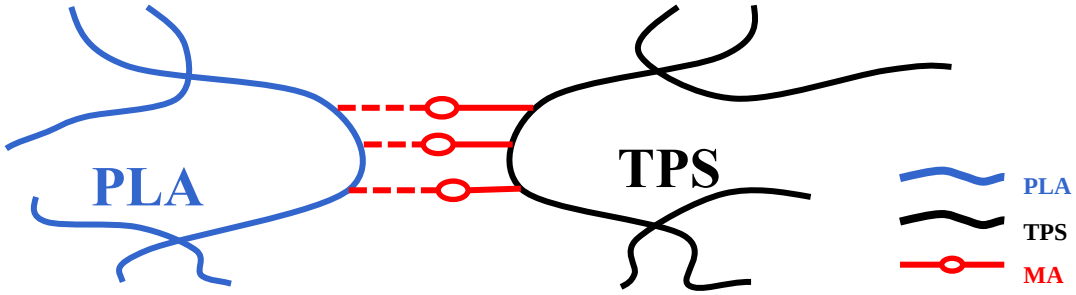


แนวคิดของการเตรียม

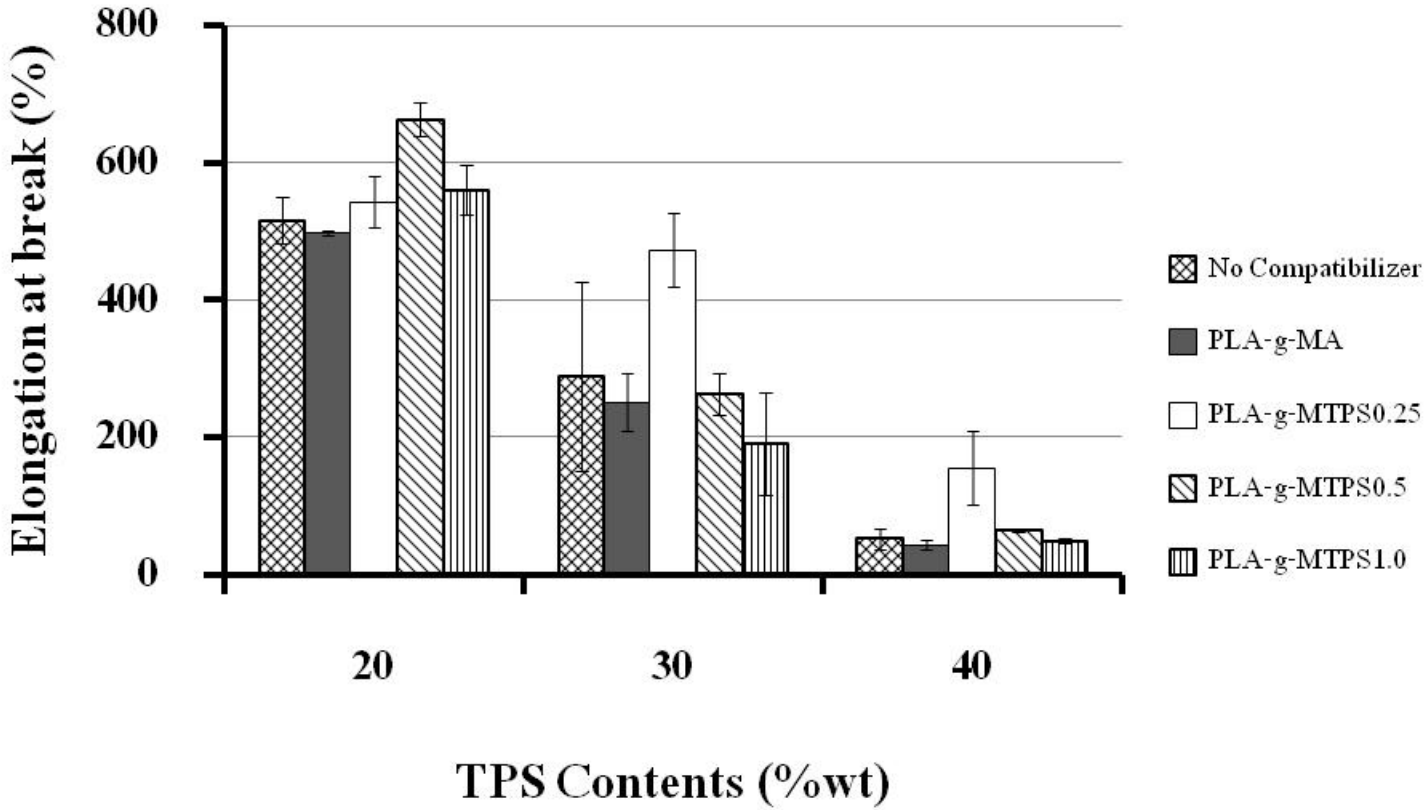
เริ่มจาก PLA-g-MA แล้วนำไปผสมกับ TPS (เกิดปฏิกิริยา trans-esterification ระหว่างผสม)



เริ่มจาก MTPS แล้วนำไปกราฟกับ PLA โดยใช้ peroxide จากนั้น นำไปใช้งานต่อเป็น compatibilizer



%Elongation at break



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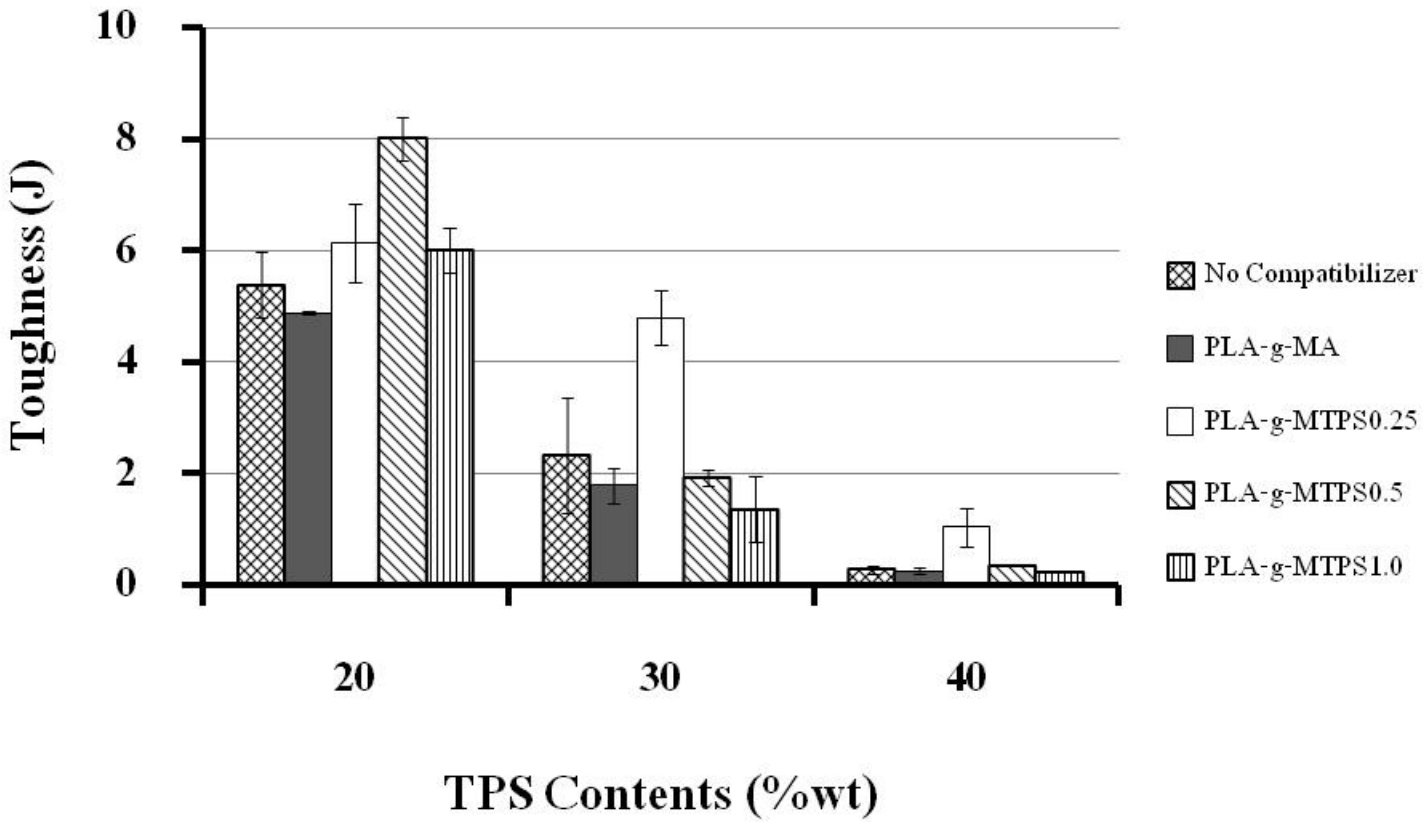
Toughness



Journal of Applied Polymer Science, Vol. 126, E388–E395 (2012)

ค่าดัชนีการไหลของพอลิเมอร์ผสม plasticized-PLA/TPS ที่ใช้ compatibilizers ชนิดต่างๆ (ทดสอบที่ 190 องศาเซลเซียส / 2.16 กิโลกรัม)

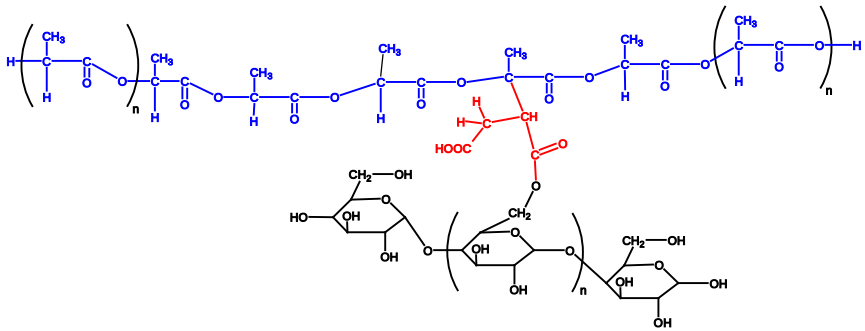
วัสดุทดสอบ	ดัชนีการไหล (g/10 min)
PLA	8.5 ± 0.5
p-PLA ที่เติมสารเปอร์ออกไซด์ 0.75 pph	8.8 ± 0.7
p-PLA/TPS (80/20 w/w) ที่ไม่มีการเติมสาร compatibilizer	19.3 ± 1.5
p-PLA/TPS (80/20 w/w) ที่มีการเติมสาร PLA-g-MA	27.1 ± 3.1
p-PLA/TPS (80/20 w/w) ที่มีการเติมสาร PLA-g-MTPS*	22.3 ± 1.7
p-PLA/TPS (80/20 w/w) ที่มีการเติมสาร PLA-g-MTPS**	17.3 ± 2.4
p-PLA/TPS (80/20 w/w) ที่มีการเติมสาร PLA-g-MTPS***	18.7 ± 2.7

หมายเหตุ * หมายถึง PLA-g-MTPS ระบบที่เตรียมโดยใช้สารเปอร์ออกไซด์ 0.25 pph

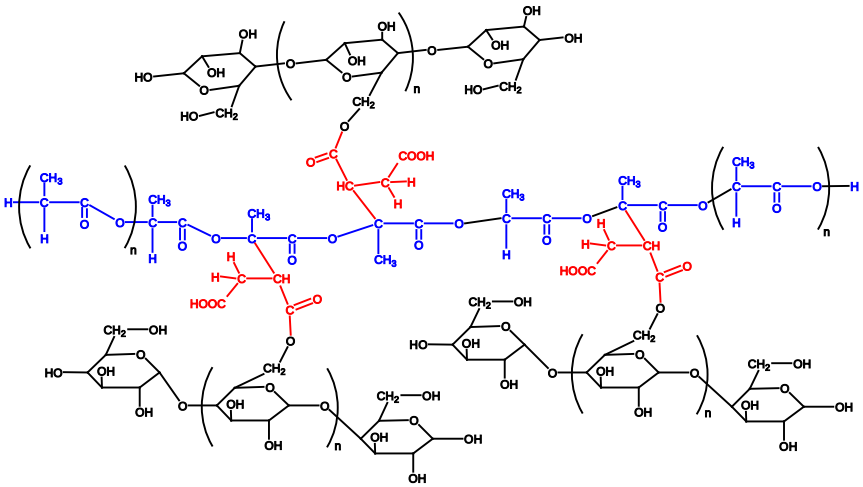
****หมายถึง PLA-g-MTPS ระบบที่เตรียมโดยใช้สารเปอร์ออกไซด์ 0.5 pph**

*****หมายถึง PLA-g-MTPS ระบบที่เตรียมโดยใช้สารเปอร์ออกไซด์ 1.0 pph**

Chemical structure of PLA-g-MTPS with various of grafting contents



Low peroxide content
Low grafting content



High peroxide content
High grafting content