

Lec-2

Commodity Resins and Their Blends

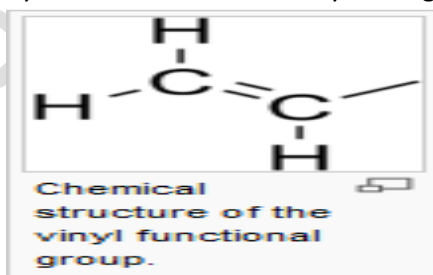
Five large-volume polymeric groups belong to this category: polyethylenes, polypropylenes, styrenics, acrylics and vinyls. Their world market share remains relatively stable — the commodity resins represent 71% of all consumed plastics.

Table 1. World Market Share (MS) and Annual Growth Rate (AGR) by Resin Type (1995-2000)

No.	Resin Type	MS (%)	AGR (%)
1.	Low density polyethylene (LDPE + LLDPE)	20	5.1
2.	High density polyethylene (HDPE)	13	5.2
3.	Polypropylene (PP)	17	6.6
4.	Polystyrene and copolymers (PS + ABS)	11	4.7
5.	Polyvinylchloride (PVC)	18	5.2
6.	Other thermoplastics (TP)	11	4.5
7.	Thermosets (TS)	10	-2.1

Notes:

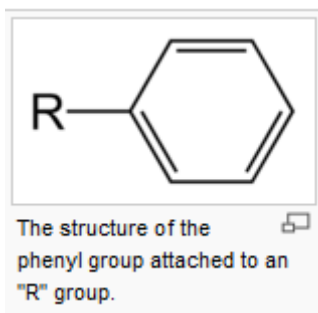
1-In [chemistry](#), **vinyl** or **ethenyl** is the [functional group](#) $-\text{CH}=\text{CH}_2$, namely the [ethylene](#) molecule ($\text{H}_2\text{C}=\text{CH}_2$) minus one [hydrogen](#) atom. The name is also used for any compound containing that group, namely $\text{R}-\text{CH}=\text{CH}_2$ where R is any other group of atoms.



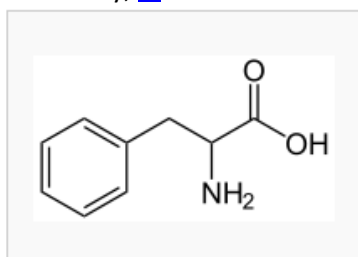
2-Vinyl polymers:

Monomer example	Example of resulting polymer
Vinyl chloride	Polyvinyl chloride (PVC)
Vinyl fluoride	Polyvinyl fluoride (PVF)
Vinyl acetate	Polyvinyl acetate (PVAc)

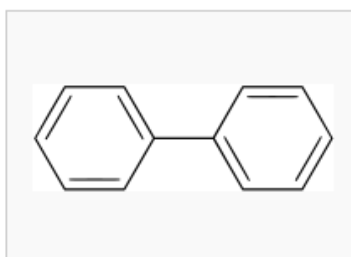
3-Phenyl group or phenyl ring is a [cyclic](#) group of atoms with the formula C_6H_5 . Phenyl groups are closely related to [benzene](#). Phenyl groups have six carbon atoms bonded together in a [hexagonal](#) planar ring, five of which are bonded to individual hydrogen atoms, with the remaining carbon bonded to a [substituent](#).



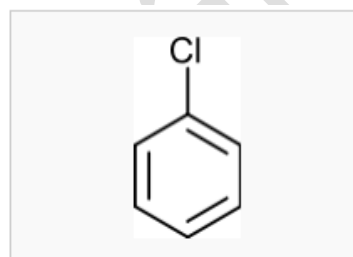
Phenyl groups often have the general formula C_nH_n [represented by the symbol](#) Ph or, archaically, Φ . Benzene is sometimes denoted as PhH.



Phenylalanine, a common amino acid.

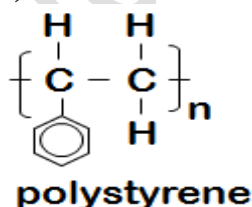


biphenyl, consisting of two phenyl groups. The two rings tend not to be coplanar.



chlorobenzene (or phenyl chloride), a solvent.

Example 1: Polystyrene (PS)



Until the 1950's, PS was produced in small quantities — the resin was brittle, thermally unstable, with poor solvent and scratch resistance. The main use of styrene was in the manufacture of styrenics, viz. *Buna-S*, SBR, or ABS.

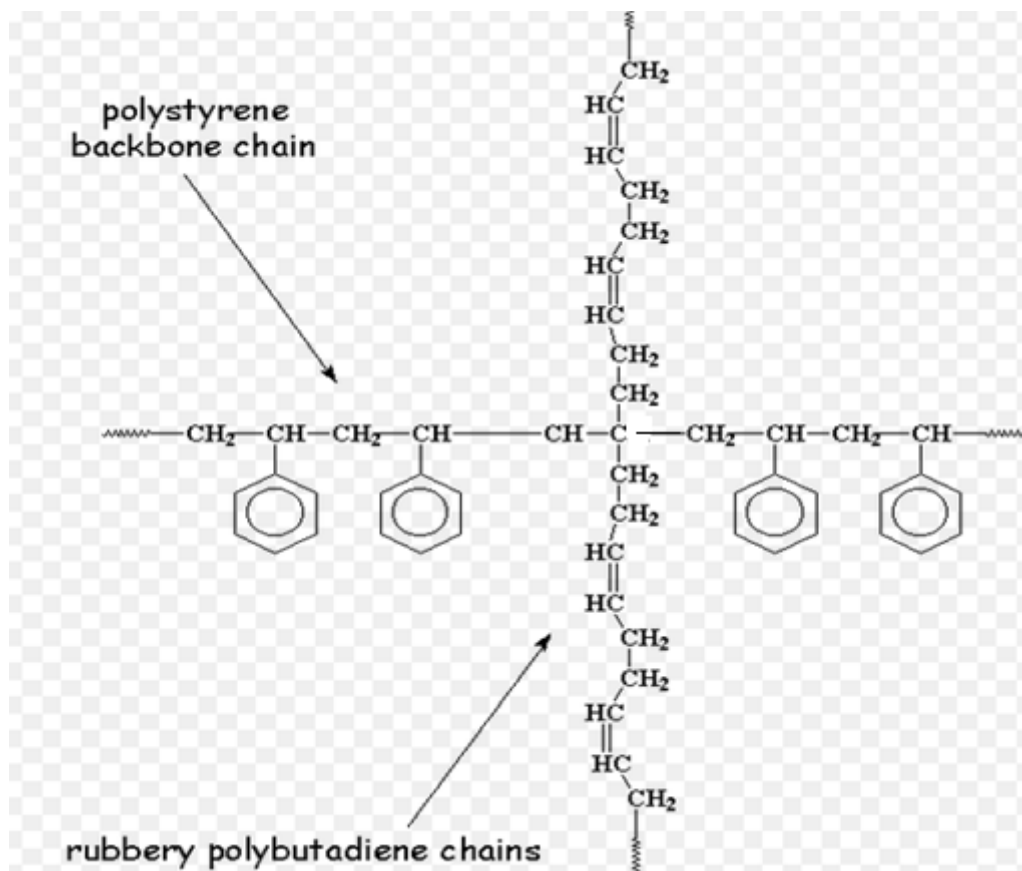
Common PS is atactic and amorphous. It has good optical clarity, low dielectric loss factor, modulus $E = 3.2$ GPa, strength $\sigma = 45\text{-}65$ MPa, density $\rho = 1050$ kg/m³, and CUT (Continuous use temperature) = 50-70°C.

Because of brittleness and low chemical resistance the demand for neat PS has decreased, and except for foaming, PS is rarely used.

PS can also be polymerized into crystalline forms: isotactic (iPS) or syndiotactic (sPS) with $T_m = 230$ or 272°C , respectively.

The high-impact PS, **HIPS**, has been known since 1911. In the USA,

Ostromislensky [1924, 1926-28] patented copolymerization of styrene with “*rubber, balata or other elastic and plastic gum*”.



HIPS product



PS is miscible with several polymers, viz. polyphenyleneether (PPE), polyvinylmethylether (PVME), poly-2-chlorostyrene (PCS), polymethylstyrene (PMS), polycarbonate of tetramethyl bisphenol-A (TMPC), etc.

PS is immiscible with PMMA, PMA, polyethylacrylate (PEA), polybutylacrylate (PBA), or PBMA

1- PS/Commodity Resin Blends

The most common immiscible PS blends are those prepared to improve the impact strength of PS or its copolymers, viz. HIPS or SBR.

Table: Toughening of PS

Composition	Reason
PS with SBR	impact performance
PS with PIB and PSIB	toughness
PS with PB and SBR	toughness
PS with SBR and a crosslinked SBR	toughness
PS with SBR and PEG	toughness, adhesion, electrostatic dissipation
HIPS (PS toughened by styrene-grafted EPR)	to improve weatherability

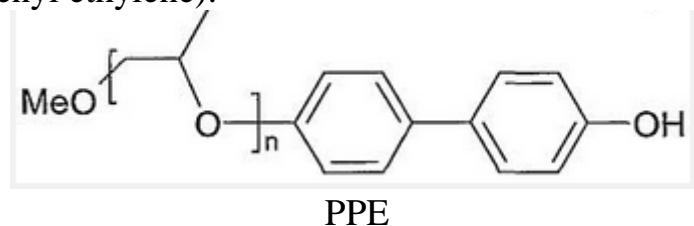
It was reported that incorporation of 0.1-18 vol% of either acrylic or olefinic elastomer particles (*e.g.*, in HIPS) into a thermoplastic (*viz.* PE, PP, PS, etc.) resulted in excellent control of the foaming process.

PS is one of the most frequently foamable thermoplastic resin. Recently blends containing ≥ 50 wt% PS (MW = 200 kg/mol) and acrylic copolymers were described as particularly useful for the manufacture of low density foams.

The presence of copolymer facilitated foaming, but it reduced the foam compressive strength. The best balance was obtained using about 22 wt% of the copolymer.

2- PS/Engineering Resin Blends

The majority of PS blends that belong to this category are mixtures with PPE (Poly phenyl ethylene).



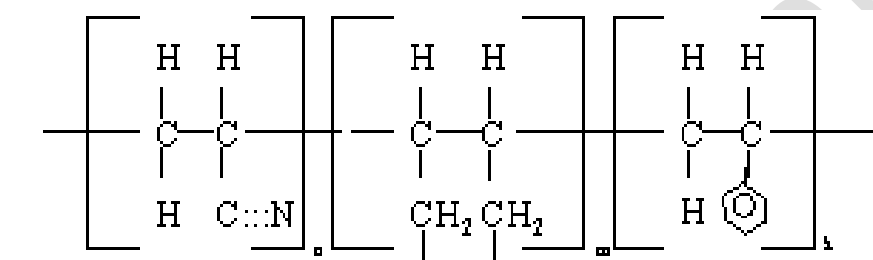
Discovery of PPE miscibility with PS led to a family of Noryl™ blends, commercialized in 1965.

The PPE/PS blends show the glass transition temperature, $T_g = 100$ to 210°C , continuously increasing with PPE content. The most often used compositions contain less than 30 wt% of PPE (PPE is about three times more expensive than PS).

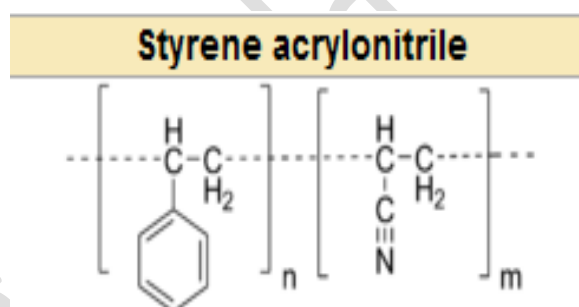
PS/PPE blends have been used as a replacement for PS in applications where higher HDT (Heat deflection temperature) and/or impact strength is required.

These alloys are easy to foam for the manufacture of, *e.g.*, hot water piping insulation, in automotive applications, etc.

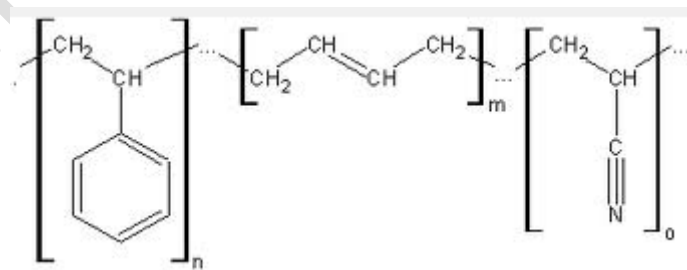
Example 2: Acrylonitrile-Butadiene-Styrene (ABS)



► The first mechanical blends of NBR with SAN (Styrene + Acrylonitrile), known as “type-A ABS,” date from 1936.



► In the mid-1940's, Dow started emulsion polymerization of “ABS type-G”.

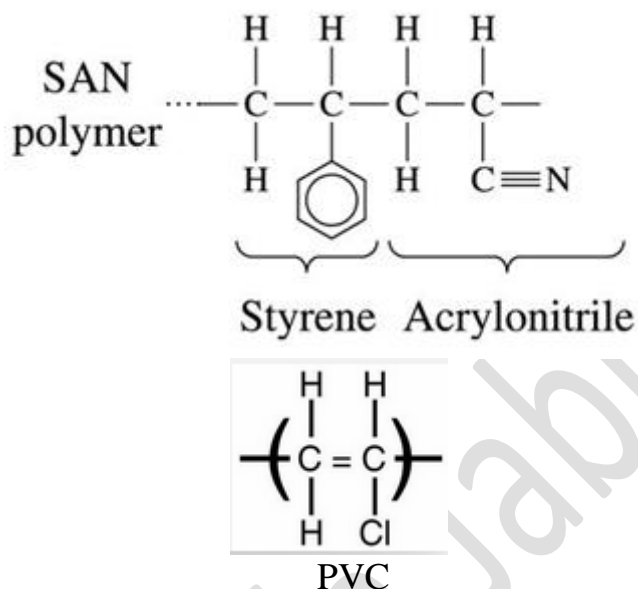


► By the late 1950's, the *high heat ABS* were invented.
 ► Weather-resistant ABS can be obtained either by the incorporation of EVAc (Ethylene-*co*-vinyl acetate), or by replacing PB with EPDM (Ethylene-*co*-propylene-*co*-diene).

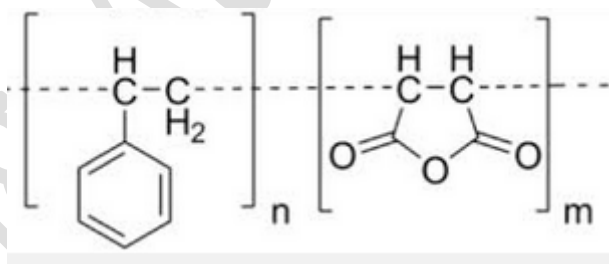
1- ABS/PVC Blends

There are several reasons for blending PVC with ABS-type copolymers, viz. to improve processability, mechanical properties, and low-temperature toughness.

Good properties of these blends originate from the miscibility between PVC and SAN-part (Styrene-co-acrylonitrile) of ABS.



In some commercial blends, viz. *Geloy*TM, ABS may be replaced by ASA (acrylonitrile-co-styrene-co-acrylate) to obtain improved miscibility and weatherability. For enhancement of HDT, SMA (Styrene-co-maleic anhydride) may also be added.



The blends with more than 30 wt% PVC are self-extinguishing, but are more difficult to process.

2- ABS/PC Blends

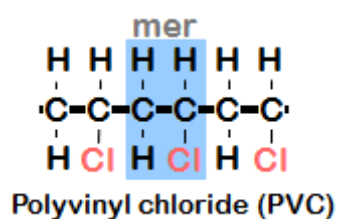
The alloys combine good processability of ABS with excellent mechanical properties, impact and heat resistance of PC.

The opaque blends show dimensional stability, low shrinkage and moisture absorption, high stiffness and hardness, good impact resistance at temperatures $T \geq -50^{\circ}\text{C}$, excellent UV stability, processability, mechanical properties, heat resistance, flame retardancy, good chemical

resistance, **but** poor to gasoline, aromatic hydrocarbons, esters, ketones and some chlorinated hydrocarbon.

There are many **similarities** between ABS/PVC and ABS/PC blends. Both are immiscible, having three distinct phases of PVC or PC, SAN, and an elastomer. The blends are compatibilized by the dipole-dipole interactions between PC and SAN, particularly evident in SAN with ≥ 25 wt% AN. ABS/PC blends can also be compatibilized by incorporation of either acrylic, acidic or epoxy groups.

Example 3: Polyvinyl chloride (PVC):



Owing to poor thermal stability of PVC, the high temperature blending must be avoided. Thus only few PVC/engineering resin blends are known.

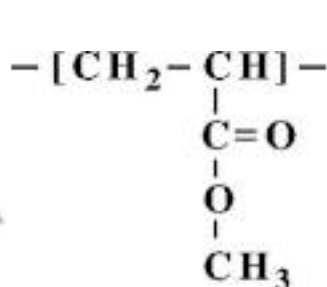
The first commercial blend of this type is *Cylon*TM. Here PVC is the matrix, and PA (that melts below 215°C!) the dispersed phase. The two resins were compatibilized using the well known PVC plasticizer — *Elvaloy*TM (a terpolymer of ethylene, carbon monoxide and acrylics).

These soft to semi-rigid alloys were commercialized for wire coating, automotive applications and blow molding. They are flame, abrasion and chemicals resistant, easy to process, and tough.

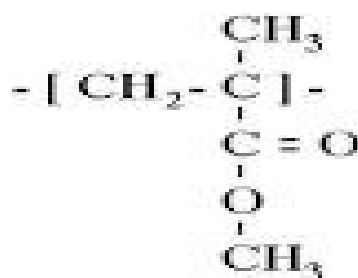
Composition	Reason for Blending
PO with PVC	for extrusion or milling
PVC with either PP, PE, PS, or SBR and ethylene-vinylchloride	HDT, flame resistance, impact and tensile strength
PVC with either PE or PP and MBS	impact strength formulations for pipes or electrical insulation

Example 4: Acrylic Blends

Polymethylacrylate (PMA) and polymethylmethacrylate (PMMA) were discovered, respectively, in 1880 and 1930.



PMA



PMMA

The resins have been used for the production of transparent plastic sheets, viz. **Plexiglas™** or **Perspex™**, used for the military aircraft cockpit canopies, gunner's turrets and the like.

Acrylic polymers are recognized for their miscibility with a variety of polymers, viz. miscibility of PMA with PVAc .

PMMA is miscible with standard PC at $T < \text{LCST}$ (lower Critical solution temperature) $\approx 140^\circ\text{C}$. The miscibility range can be greatly increased by modifying the PC chain ends ($\text{LCST} \leq 300^\circ\text{C}$). PMMA is also miscible with fluorinated-PC.

► Impact Modification of PMMA

PMMA, like PS, is brittle and requires toughening. These efforts are summarized in Table below:

PMMA Impact Modifier

PVAc

Copolymers of methacrylonitrile, ethylacrylate and/or α -methylstyrene

Ethylene-vinyl acetate-vinyl chloride copolymer (EVAc-VC)

SMA and methylmethacrylate-methylacrylate copolymer (MMMA)

MBA: copolymer of butadiene, butylacrylate and methylmethacrylate

Styrene-acrylonitrile copolymer (SAN)

SAN, PS, and poly(methyl norbornene-2-carboxylate)

► PO Blends with Acrylic Polymers

PMMA is antagonistically immiscible with a polyolefins — blends of this type have been used in non-critical applications, viz. PP/PMMA blends with EVAc were used as plastic-paper, while those with PVC as wood-like materials

Note:

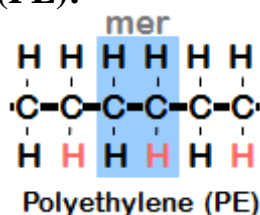
A **polyolefin** is a [polymer](#) produced from a simple [olefin](#) (also called an [alkene](#) with the general formula C_nH_{2n}) as a [monomer](#). For example, [polyethylene](#) is the

polyolefin produced by polymerizing the olefin [ethylene](#). An equivalent term is **polyalkene**; this is a more modern term, although polyolefin is still used in the [petrochemical](#) industry.^[1] [Polypropylene](#) is another common polyolefin which is made from the olefin [propylene](#).

► **POM Blends with Acrylic Polymers.** These systems are not of industrial importance. However, addition of an acrylic was reported to improve processability, abrasion resistance, and weatherability of POM.

For example, to improve weatherability POM was blended with polythioisocyanate, TPU, PMMA, and benzotriazole.

Example 5: Polyethylenes (PE):



Properties of PE depend on: molecular weight (MW), molecular weight distribution (MWD), as well as on the degree and type of branching. The density and modulus of PE's increase with crystallinity.

Table : Polyethylenes

No	Type	Code	Density (kg/m ³)	Characteristics
1	Ultra-High-MW	UHMWPE	$\rho \approx 969$	MW > 3,000 kg/mol
2	High density	HDPE	941-969	High MW and crystallinity
3	Medium density	MDPE	926-940	
4	Low density	LDPE	910-925	Long chain branching, $T_m = 115^\circ\text{C}$
5	Linear low density	LLDPE	910-925	Ziegler Natta type with short branching, $T_m = 120-135^\circ\text{C}$
6	Very low density	VLDPE	900-910	
7	Ultra low density	ULDPE	855-900	$T_m = 40-85^\circ\text{C}$

PE/Elastomer Blends:

Polyolefins have been modified by the incorporation of elastomers to improve low temperature impact strength and elongation.

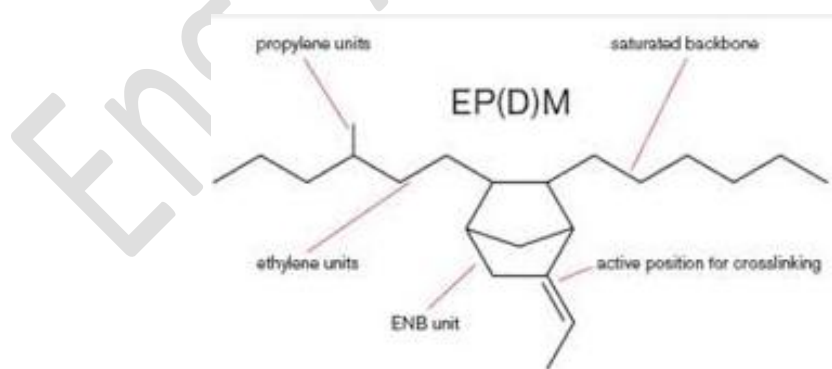
Modifier	Reason
Rubber	impact modification
Cyclo-rubber	adhesion to metal
PIB	transparent, impermeable, shrink-wrap films
CSR	for films or coatings
BR	improve elongation

PE/PE Blends:

Blend	Advantage
LDPE with LLDPE	processability, stiffness, abrasion resistance, H ₂ O vapor permeability
LDPE, HDPE and EPDM or aPP	soft, thin films
Two types of LLDPE	processability, impact strength, mechanical performance
LLDPE with: LDPE, PP, TPO's, rubbers, EVAc, PP-MA, EPR, ...	improved processability
HDPE with LLDPE	improved strength and transparency

PE/PP Blends:

PE has been used to improve the low temperature impact strength of PP. The blends are mostly immiscible, compatibilized either by addition of EPR, EPDM, by reactive blending, or by post-blending co-crosslinking, *e.g.*, by electron beam or γ -radiation.



PE/PA Blends:

The reasons for blending PE with PA are:

- 1-A desire to improve the impact strength and moisture absorption of PA
- 2-To improve rigidity & barrier properties (to oxygen & solvents) of PE

PE/PC Blends:

To increase rigidity of PE, the resin has been blended with about 5 wt% of a high-modulus polymer, *e.g.*, PC . PC also stabilized PO against the thermal degradation.

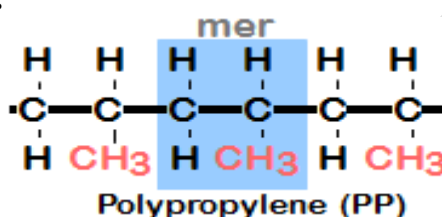
PE/Specialty Resin Blends:

Most specialty resins are processed at temperatures that limits the possibility of blending them with PE. The PE/specialty resin blends usually contain low concentration, ≤ 5 wt%, of either component.

Addition of PE improves the processability, surface finish, chemical, solvent and impact resistance.

Addition of specialty polymer to PE may improve rigidity and processability.

Polypropylene (PP):



There are three types of polypropylene: amorphous (aPP), isotactic (PP), and syndiotactic (sPP). Performance of these resins depends on the tacticity content.

The advantage of sPP over PP is that impact strength and tensile modulus of sPP are significantly higher. While PP has a planar zigzag helical structure, the sPP has a three-dimensional one that leads to lower crystallinity and melting point: $T_m(\text{PP}) \approx 165$ vs. $T_m(\text{sPP}) \approx 133^\circ\text{C}$.

PP is brittle, especially at $T \leq T_g \approx 0^\circ\text{C}$. The resin fractures by the crazing-cracking mechanism .

The discovery of PP immediately followed by search for methods of improvement the low-T impact behavior. PP was blended with: EPR or EPDM.

The PP/EPR blends can be processed by all methods used for PP. They are characterized by good processability, dimensional stability, low shrinkage, high stiffness, tear strength and softening temperature, good mechanical properties (at $T = -40$ to 150°C), ozone resistance, fatigue and abrasion resistance .

These materials have been used in more than 200 applications, in automotive industry, appliances, hardware and plumbing, medical, shoe industry, sports equipment, toys, etc

Elastomer Added To PP	Comment
PP with 18-32 wt% EVAc and/or ethylene-ethylacrylate copolymer (EEA)	impact strength, elongation, and low-T brittleness
PP with EVAc	dyeability, flexibility, barrier properties, and toughness
PP/EVAc and POM, PMMA, PS or SMM	for paper-like films

► PP/Specialty Polymer Blends

Most specialty resins require high processing temperatures, while PP usually has $T_{\text{proc}} < 250^{\circ}\text{C}$.

Thus, only few blends of this type are known, none commercial.

PP blends with a small amount of LCP(Liquid Crystalline Polymer) are of industrial interest for two reasons:

- 1-To improve processability
- 2- To improve the mechanical performance.

Table : PP/LCP blends

Composition	Comment
Low concentration of LCP in a resin	to improve processability
10 wt% of LCP was blended with, <i>e.g.</i> , PP, PS, PC or PI	molecular orientation imposed by extrusion through a rotating die
LCP &: PP, PET, PA, PC, PE, PVC, PVDC, PPS, PVDF, PVF or PMMA	to produce oriented films with protrusions that resulted in low friction
PP was blended with LCP	2 extruders with a static mixer, to stretch LCP into microfibrils
PP/LCP compatibilized with PP-MA	(processing as described above)
LCP with either: PP, PPE, PPE/PS, PC, PEI, etc.	(1) preregs from an extruder, mixer, and rolls; (2) preregs consolidated at $T < T_m$.