EFFECTS OF POLYSTYRENE-MODIFIED

NATURAL RUBBER

ON THE PROPERTIES OF

POLYPROPYLENE/POLYSTYRENE BLENDS

by

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LIST OF ABBREVIATIONS

4 ssa,ssh	-	sodium salt hydrate of 4 styrenesulfonic acid
ABS	-	Arylonitrile butadiene styrene
BDA	-	1, 4-Butanediol diacrylate
DPNR	-	Deproteinized Natural Rubber
DSC	-	Differential Scanning Calorimetry
ENR	-	Epoxidized natural rubber
EPDM	-	Ethylene-propylene-diene rubber
EPDM-g-SAN	-	Ethylene/propylene/diene elastomer grafted with SAN copolymer
EPR-g-MA	-	Maleic anhydide grafted ethylene-propylene copolymer
ESCR	-	Environment stress cracking resistant
EV	-	efficient sulfur recipe
EVA	-	Ethylene-vinyl acetate copolymer
HIPS	-	High impact polystyrene
IPPD	-	N-Isopropyl-N-phenyl-p-phenyllendiamine
IR	-	Ignition resistant grade
MBTS	-	Dibenzothiazol disulfide
NBR	-	Nitrile butadiene rubber
NR	-	Natural rubber
OsO_4	-	Osmium tetraoxide
PB	-	Polybutadiene
PBA	-	Poly (n-butyl-acrylate)
Pet.ether	-	Ethyl acetate and petroleum ether
PF	-	Phenolic formaldehyde
PMMA	-	Polymethyl Methacrylate

PP	-	Polypropylene
PS	-	Polystyrene
PPA	-	Phenoxy Ethyl Vinyl Ether Grafted PP
PVC	-	Poly (vinyl chloride)
SAN	-	Styrene-acrylonitrile
SEBS	-	Poly (ether ester) /Polystyrene and styrene/ (ethylene-butylene) based block copolymer
SEBS-g-MA	-	Styrene-(ethylene-co-butylene)-styrene triblockcopolymer
SEM	-	Scanning Electron Microscopy
SEP	-	Poly (styrene/ethylene-propylene)
SIS	-	Surface imaging analysis system
SNR	-	PS-modified NR
SPS	-	Syndiotactic polystyrene
THF	-	Tetrahydrofuran
TMTD	-	Tetramethylthiuram disulfide
TPE	-	Thermoplastic Elastomer
TPO	-	Thermoplastic olefin

LIST OF MAIN SYMBOLS

α_C	-	critical stress in a centrally loaded and simply supported beam (three point bending)
α_{max}	-	maximum stress
α_y	-	yield stress in a centrally loaded and simply supported beam (three point bending)
a°	-	intrinsic flaw size
A_1	-	mass of styrene monomer used for the polymerization reaction
A_2	-	mass of non-reacted styrene
B	-	sample depth
D_n	-	number-average diameter of particles
E	-	Young's modulus
E_B	-	elongation at break
E_f	-	flexural modulus
I	-	impact strength
M_1	-	mass of extract
M_{100}	-	modulus at 100 elongation
M_2	-	mass of specimen used
M_A, M_B	-	molecular weight of each homopolymers
M_{eA}, M_{eB}	-	the total entanglement of molecular weights of the two homopolymers
P_c	-	load at failure
P_{gy}	-	the load at the general yield point
S	-	beam span
t_{90}	-	optimum cure time
T_{max}	-	maximum torque

T_{min} -   minimum torque

TS   -   tensile strength

U   -   elastic energy

U_c -   elastic energy at critical stage

U_p -   elastic energy corresponds to the area

U_y -   elastic energy at yield point

U_y^* -   elastic energy for ductile behavior Type B

V_1 -   value of the property after aging

V_2 -   value of property before aging

W   -   sample width

w_p -   work done in deforming the bar plastically

X   -   deflection at the center of the beam

X/S   -   deflection to-span ration

X_c -   rupture of the bar occurs at a critical deflection to-span ration

X_p -   the deflection subsequent to general yield

ABSTRAK

SNR, yang mengandungi 25% Polistirena (PS) dan 75% getah mengikut jisim dan 80% daripada PS tergraf pada getah, telah disediakan dalam makmal. Proses-proses termasuk penambahan air, latek, monomer dan pemula mengikut resipi. Masa tindakbalas adalah 5 jam pada suhu 60^oC. Nisbah Stirena: Getah adalah 25:75 mengikut jisim dan Kandungan Pepejal Mutlak (TSC) dalam reactor adalah 40% termasuk Kandungan Pepejal Mutlak (TSC) bagi latek DPNR, stirena dan pemula.

Adunan polipropilena (PS), sejenis polimer separa-hablur, dengan polistirena (PS), polimer amorfus, diketahui tidak terlarutcampur. Kajian ini melaporkan peningkatan dalam sifat-sifat mekanikal bagi adunan PP/PS 80/20 apabila ditambah dengan getah asli terubah suai stirena (SNR) sebagai penyerasi. Beberapa adunan PP/PS, pada pembebanan 0%, 2.5%, 5%, 7.5%, dan 10% SNR, telah disediakan secara pencampuran lebur dengan menggunakan Mesin Brabender Plasticorder dengan halaju skru 50bpm pada suhu 185 ^{o}C. Fasa getah asli dimatangkan secara dinamik menggunakan satu resipi pematangan sulfur yang biasa.

Adunan PP/PS pada 5% SNR mengikut jisim memberikan kombinasi terbaik kepada sifat-sifat mekanikal. Kekuatan tensil meningkat dari 20MPa kepada 24MPa dan terikan pada takat putus dari 13% kepada 370%. Kekuatan impak meningkat dari 198 kJ/m kepada 391 kJ/m dan selaras dengan peningkatan keliatan rekahan, Kc, dari 3.85 MPa/m^2 ke 3.97 MPa/m^2. Keujudan deformasi plastik bagi adunan dengan 2.5% dan 5% SNR mengikut jisim menunjukkan ada interaksi yang baik antara fasa PP dan PS. Beberapa permerhatian secara morfologi dengan Pemskanan Elektron Mikroskopi (SEM) juga menyokong kesan penyerasian untuk adunan PP/PS dengan SNR. Perbandingan beberapa penyerasi komersil dengan SNR dalam adunan PP/PS juga memberi maklumat positif tentang kebaikan SNR. Keputusan mencadangkan bahawa getah asli dalam bentuk terubah suai stirena boleh menjadi penyerasi yang berkesan untuk adunan PP/PS.

ABSTRACT

SNR, which contained 25 % PS and 75 % rubber by weight and with 80% of the PS grafted onto the rubber, was prepared in the laboratory. The processes include addition of water, latex, monomer and initiator according to the recipe. Reaction time was 5 hours at 60°C. Styrene: rubber ratio is 25:75 by weight and the total solid content (TSC) in the reactor was 40% which included TSC for DPNR latex, styrene and initiator.

Blend of polypropylene (PP), a semi-crystalline polymer, with polystyrene (PS), an amorphous one, is known to be immiscible. This study reports on the improvement in mechanical properties of 80/20 PP/PS blend when incorporated with highly grafted styrene-modified natural rubber (SNR) as a compatibilizer.. Various PP/PS blends at 0%, 2.5%, 5%, 7.5%, and 10% loading of SNR were prepared by melt-mixing with the screw speed of 50 rpm at 185°C. The rubber phase was dynamically vulcanized using a typical sulfur curing recipe.

The PP/PS blend at 5 wt % of SNR gave the best combination of mechanical properties. The tensile strength was increased from the 20MPa to 24Mpa and the strain at break from 13% to 370%. The impact strength was improved from 198 kJ/m to 391 kJ/m and consistent with increase in the fracture toughness, Kc, from 3.85 MPa/m^{2} to 3.97 MPa/m^{2}. The existence of plastic deformation for blends with 2.5 wt % and 5.0 wt % of SNR indicates that there is a good interaction between the PP and PS phases. Some morphological observation by Scanning Electron Microscope (SEM) analysis also supports the compatibility for the PP/PS blend with SNR. Comparison between a few commercial compatibilizer with SNR in PP/PS blend also provide a positive insight to the advantages of SNR. The results suggest that natural rubber in the styrene-modified form could be an effective compatibilizer for PP/PS blends.

CHAPTER 1
INTRODUCTION

1.1   Polymer blends

Polymer blends or alloys have been the subject of intense study for a long time, but in the recent years, totally immiscible blends are of interest to many polymer researchers with respect to making such blends/alloys compatible. The term blends and alloys are often used interchangeably but in this work, the terminology by Utracki [1989a] has been adopted. Blending is an attractive method of creating new materials with improvement and flexibility in performance, and better properties than existing polymers [Utracki, 1982].

The definitions of polymer blend vary from a brief description to a specific one. Polymer blends of dissimiliar properties are of considerable technological importance as the blending provides means to improve physical properties such as toughness and processibility. Utracki [1989b] stated that a polymer blend is a mixture of two or more polymers or copolymers and as a mixture containing ≥ 2 wt% of two or more macromolecular species. These preparation methods do not usually lead to chemical bonding between the components. Polymer blends are physical mixture of two or more polymers and are commercially prepared by mechanical mixing which is achieved through screw compounder and extruder. Blending these components leads to two-phase or multiphase morphologies [Wallheinke et. al, 1998].

From the various definitions above, it can be concluded that polymer blend is simply a mixture or combination of polymers (homopolymers or copolymers) obtained through various processing techniques. Ideally, two or more polymers may be blended

together to form a wide variety of random or structured morphologies to obtain products that potentially offer desirable combinations of characteristics.

1.1.1   Polypropylene Blends

Polypropylene is a linear hydrocarbon polymer containing little or no unsaturation as shown in Figure 1.1. It is a highly crystalline thermoplastic that exhibits low density, rigidity and good chemical resistance to hydrocarbons, oxidizing agents, alcohol. One of the major characteristic that is attractive for blending is the excellent impact balance [Myer, 2002].

$$-\!\!\left[CH_2-CH\right]_n$$
$$CH_3$$
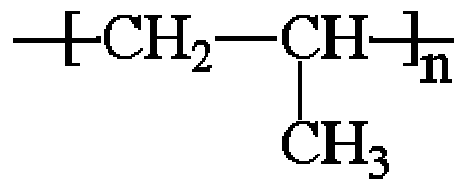
Figure 1.1: Structure of Polypropylene

The existence of a methyl group attached to alternate carbon atoms on the chain backbone give a slight stiffening of the chain and it can interfere with the molecular symmetry. The first effect leads to an increase in the crystalline melting point whereas the interference with most significant would tend to depress it [Brydson, 1999]. Tacticity in layman term is the way pendant groups are arranged along the backbone chain of a polymer. Due to its crystalline characteristic, polypropylene is soluble only at elevated temperature which the same like any other crystalline polyolefin. The crystallinity will decrease with increasing temperature. Typical uses of polypropylene include sterilizable hospital items, dished, appliance parts, dishwasher components, container automotive

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ducts, trim, etc. The miscibility mixture of amorphous and semi-crystalline polymers is limited to the melt and amorphous phase. On cooling, the semi-crystalline polymer partially separates and crystallizes [Utracki, 1982].

Blends of PP and ethylene-propylene rubber (EPR), ethyl-propylene diene monomer (EPDM), styrene-butadiene-rubber copolymer (SBS), polyisoprene have been commercialized for automotive applications such as bumper and dashboards [Mattiussi & Forcucci, 1990]. Blends with small amount of rubber are a toughened version of PP, while those with majority of EPR are thermoplastics elastomers. With proper selection of composition, a wide variety of stiffness, toughness and other physical properties can be obtained. In order to improve low temperature impact performances, PP has also been toughened by incorporating HDPE or LLDPE into the blend.

Blending of PP with elastomers such as EPM, SBS, EPDM, SIS, PIB and polyisoprene will affects both the morphology and the crystallization behavior of PP [Martuscelli, 1990]. It was also reported that EPDM and EPM were found to be more chemically compatible with PP comparing to other elastomers. Basically, elastomers decrease the degree of crystalline portion of PP and the average spherulite size which contribute to an improvement in the impact strength.

It has been suggested that some degree of crosslinking of the rubber modifier phase is necessary to improve the toughening effect of the rubber. Ong [2002] & Elliot [1990] in their work on PP/NR (natural rubber) blend found substantial improvement in impact strength for slightly crosslinked NR compared to uncrosslinked NR phase.

1.1.2 Polystyrene Blends

Polystyrene has a very simple repeating structure as shown in the Figure 1.2 below. It is an atactic polymer thus is regarded as amorphous. This commercially available thermoplastic has been around for quite sometime. The specific location of the benzene ring is sufficiently random to inhibit crystallization [Brydson, 1999b].

$$\left[CH_2-CH \right]_n$$
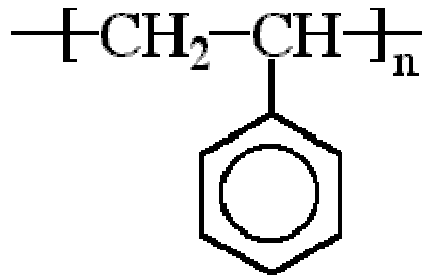
Figure 1.2: Structure of Polystyrene [Brydson, 1999b]

Polystyrene is a hard, crystal clear, amorphous solid at room temperature that exhibits high stiffness, good dimensional stability, moderately high heat deflection temperature and excellent electrical insulating properties [Myer Kutz, 2002]. It retains its stiffness to about 20-25°C below glass transition temperature (Tg). However, polystyrene will become softer as it getting closer to its Tg which is around 100°C. Above Tg, polystyrene behaves under stress as a viscous fluid. When the temperature is further raised, it will become rubbery and highly extensible. Polystyrene is easily processed by all normal thermoplastic processes to produce common applications such as wall tile, electrical parts, lenses, bottle caps, transparent display boxes, etc. However, it is brittle under impact and the resistance towards surfactants and solvent is very poor [Myer Kutz, 2002].

Early attempts to improve the impact properties of PS without loss of transparency failed [Utracki, 1998]. In 1959, Mosanto announced that by blending PS with polyethylene (1-10wt% PE) and chlorosulfonated-polyethylene could produce a blend of PS with improved impact, elongation and strength.

The blends of PS with polycarbonate of bisphenol-A (PC) are immicible but since many copolymers show good affinity with both resins, blend of PC with styrenics were developed relatively earlier. Similar to findings by Ong [2003], PS/NR with slightly crosslinked rubber phase improves the impact resistance of PS compared to uncrosslinked NR as found out by Neoh [2003].

1.2   Compatibility and miscibility

The terms *compatible* and *miscible* are often used casually and indiscriminately giving rise to some confusion and ambiguity. The term *miscible* is used to describe polymer blends that have theoretical thermodynamic miscibility down to the segmental or molecular level whereas the term *compatible* is used to describe polymer blends that have useful practical properties, regardless of whether they are theoretically miscible or immiscible [Utracki, 1990]. Blends do not have to be miscible to be useful. Most commercially important polymer blends are immiscible but are compatibilized through interfacial modification. Acceptable overall physical and mechanically properties of an immiscible but compatibilized blend should be related to low interfacial tension and strong adhesion between the phases. Blends of this type are termed 'compatible' even though in a thermodynamic sense they are in actual not miscible. Compatible blends are characterized by the presence of a finely dispersed phase, good adhesion between blend

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phases, strong resistance to phase coalescence resulting in technologically desirable properties.

For example, although the PP/PS blends system presented in this study is known and has been reported to be theoretically immiscible [Krause, 1978]; it could be rendered compatible by addition of a suitable comptabilizer, the resultant blend produces excellent properties that are useful. Thus, in this research presentation, a blend is considered compatible if it exhibits a set of properties which are desirable and useful, regardless of whether the blend has complete or partial miscibility, or due to the application of a suitable compatibilization technique.

1.3   Problem Statement

Blends of isotactic polypropylene (PP) and atactic polystyrene (PS) are immiscible over the whole composition range and they have, consequently, poor mechanical properties [Krause, 1978; I.Smit et al, 2004]. PP is a semi-crystalline plastic whereas PS is an amorphous plastics and both exhibit different type of applications and characteristics. PP is a versatile plastics but brittle especially in low temperature. PP has been toughened by blending with HDPE or LLDPE to improve its low temperature impact performances [Blom *et. al*, 1989]. An amorphous plastic such as PS on the other hand is very sensitive to temperature above its Tg (around $100^{o}C$) which cause it to become rubbery and soft. Ideally, two or more polymers may be blended together to achieve desirable combinations of characteristics and in this case is PP and PS blends. PS is a hard polymer and is useful in increasing the rigidity of PP/PS blends whereas PP is useful for higher temperature applications and grease resistance [Karger-Kocsis, 1995]. PP is also good for blending as it can improve processibility [Utracki, 1998]. The main obstacle however is to create a compatible blend of PP/PS with a good balance of mechanical properties.

There have been a few studies reported on PP/PS blends especially on improving the compatibility of the blends. One of the more conventional methods and effective way for compatibilization of two polymers is by introducing the third component as compatibilizer in the blend [Yong Wang *et al*, 2002; Datta S et al, 1996; Koning C et al, 1998]. Block or graft copolymers (with the same or similar structure to blend components) are recommended as they are suitable as compatibilizer [Paul & Newman, 1978]. There are many types of compatibilizer that have been reported to have positive impact on PP/PS blends [Halimatuldahliana et al, 2002; Mustafa, 2003].

Halimatuldahliana reported that incorporation of commercially available SEBS as compatibilizer in PP/PS blends improves the impact properties. Mustafa on the other hand uses laboratory-made PP-g-PHEVE (phenoxy ethyl vinyl esther grafted PP) as a compatibilizer in PP/PS blends and reported improvement in some of the mechanical properties and also significant compatibilization formed between PP and PS phases.

The study reported here is an investigation of blends of PP with PS with PS-modified natural rubber (SNR) through dynamic vulcanization. This research is based the approach of rubber toughened plastics point of view with regard to the limited amount of rubber used. SNR is a high molecular weight material which is different from other reported compatibilizers as they are either plastic based or rubber based compatibilizer with relatively low molecular weight. High molecular weight compatibilizers such as SNR are useful as they are expected to minimize the loss of important mechanical properties such as tensile strength and modulus (stiffness) in polymer blends. Since SNR is also a rubber, it is expected to improve the ductility and the impact resistance in the PP/PS blend. It is also expected that SNR will act as a good compatibilizer in which the styrenic portions is compatible with PS and natural rubber component would interact with the methyl group in PP. Morphologically, it is also expected both PP and PS phases to be better dispersed compared to uncompatibilized PP/PS blend. By comparing PP/PS/SNR blends with other compatibilized PP/PS blends, the effect of laboratory made SNR on the blends' properties could be compared and evaluated.

The objectives of this study are:

1) To study the effect of SNR on the mechanical properties of 80/20 PP/PS blends.

2) To study the effect of SNR as a compatibilizer on the morphology and thermal properties of PP/PS blends.

3) To evaluate the effectiveness of SNR as a compatibilzer with reference to a few other compatibilizers on PP/PS blends based on literature findings.

1.4   Outline of Thesis Structure

Chapter 1 starts with the application and processing of PP and PS followed by the concepts of miscibility and compatibility of plastics blends as well as the types/methods of blending available today. The problem statement, primary objective and the general flow of the whole research program are also outlined.

Chapter 2 relates the role of rubber, compatibilizer, and dynamic vulcanization process on plastic-rubber blends. The internal elastic energy is also stated. Subsequently, a literature survey on various PP/PS blends with compatibilizer is presented, particularly those that are closely related to this work.

Chapter 3 describe step-by step the experimental procedures employed, details of lab equipments used as well as the processing techniques involved in generating any data that were used and presented in the course of the study.

Chapter 4 reports the properties of and characterization of SNR such as degree of conversion and sol-gel analysis, cure characteristic, morphology and tensile properties. The processing of the PP/PS and PP/PS/SNR blends are also described and how PP/PS 80/20 blend is chosen to be studies further in this work. The study SNR as compatibilizer

and the comparison with commercial types and also lab synthesized type are reported as well with regards to PP/PS blends particularly PP/PS 80/20.

Chapter 5 presents some concluding remarks on the present work as well as some suggestions for future work.

CHAPTER 2
LITERATURE REVIEW

2.1 Rubber-toughened plastics

Various plastic grades available in the market possess useful end properties and other advantages such as ease of processibility and recyclability. However, they are often brittle and have low impact strength due to the high glass transition temperature and/or degree of crystallinity [Wang *et al*., 1996]. To overcome the brittleness drawback and to improve the impact strength, the plastics could be toughened by incorporation of rubber. Modification of brittle polymer (e.g. polystyrene, polycarbonate, epoxy) by rubber is an efficient way for material toughening [Bucknall, 1977; Paul and Newman, 1978a; Ishikawa *et al*., 1996].

2.2 High impact polystyrene

One of the well known commercial rubber toughened plastics for good impact application is high impact polystyrene (HIPS). In the late 1940s, Amos et al. produced the first modern high-impact polystyrene (HIPS) [Amos et al., 1954]. HIPS is made by polymerization of an unsaturated rubber dissolved in styrene in a solution or mass suspension process [Middlmann, 1977; Daoud *et al*. 1975]. Both polystyrene and poly (butadiene-g-styrene) are formed. The graft copolymer concentrates at the phase boundary, where it acts as a surfactant. After phase inversion, polystyrene becomes the continuous phase and polybutadiene the dispersed phase [Bucknall, 1977]. The table 2.1 shows the typical recipe for toughened polystyrene [Bucknall, 1977].

Table 2.1: Typical recipe for toughened polystyrene

Recipe	Part per hundred
Styrene monomer	92.0
Polybutadiene	8.0
Benzoyl peroxide (initiator)	0.05
Dicumyl peroxide (initiator)	0.05
Tertiary idecyl mercaptan (chain transfer agent)	0.20

Other methods of preparing HIPS also have been studied. High-impact polystyrene is prepared on a novel one step method in which the starting elastomer is present as latex but the finished resin is covered as suspension beads [Shirley, 1975]. The reaction is initiated by either oil-soluble or water-soluble catalysts. Evidence is presented to show that polymerization begins when the system is still in the latex phase even when an oil-soluble suspension catalyst is used exclusively.

There are various grade of HIPS in the market such as extrusion, injection grade, high heat, high melt flow, high gloss, environment stress cracking resistant (ESCR), and ignition grade (IR) [Soderquist *et al.*,1970]. The properties of conventional and specialty commercial grade of HIPS are shown in Table 2.2. The HIPS which has occluded PS, stress whitening, copolymers/ or grafting and cross linked rubber particles with rubber particles size in the range of 2-5 µm, usually has a 10-fold increase in elongation and several-fold increase in impact strength over unmodified PS. [Boyer *et al.*,1970].

Table 2.2: The properties of conventional and specialty commercial grade of HIPS

[Soderquist *et al*., 1970]

Properties	Extrusion	Injection Molding	High Heat	High Melt Flow	High Gloss	ESCR	IR
Tensile Rupture, MPa	16.6	15.6	20.7	17.9	23.0	17.2	15.2
Tensile Yield, MPa	17.9	18.6	22.1	22.8	25.5	13.8	20.0
Tensile modulus, MPa	1655	1793	1793	2207	2241	-	1862
Elongation, %	40	40	40	20	20	30	25
Flexural modulus, MPa	1931	1793	1793	2276	2138	-	-
Flexural strength, MPa	38.6	32.4	41.7	42.8	51.7	-	-
Notched Izod At 23°C, J/m	80.1	86.5	85.5	37.4	122.8	74.7	74.7

In experiments on HIPS containing small rubber particles has showed that rates of crazing were high, and continued to increase throughout the test [Soderquist et al., 1970]. Besides, the impact strength and elongation at break also low. These results offer

strong support for the view that small rubber particle unable to stop the initiated craze from the neighbouring particles.

The void formation in the rubber particles increases the energy dissipation on impact [Ramsteiner *et al*., 2002a]. This shows that by thermal cross-linking of rubber particles in HIPS, has reduce the ability of rubber particles to cativate. Adding adequate oil in HIPS, has facilitates void formation. HIPS (rubber content: 7% by wt) with 4% oil has increase the impact strength from 27 to 31 kJ/m^2 . It can be concluded that crazing/ shearing are facilitated, if the rubber particles can easily cavitate.

The factors controlling the rubber efficiency in impact polystyrene is due to the amount of rubber phase volume (rubber + occluded PS), the degree of cross-linking of the rubber, and the molecular weight distribution of the matrix PS [Wagner and Robeson, 1970]. As the rubber phase volume increase at constant rubber concentration, impact strength and ultimate elongation pass through maxima. Over cross linking of the rubber and a high concentration of the low molecular weight of matrix PS have deleterious effect on the impact strength and ultimate elongation.

2.3 The factors controlling the rubber efficiency

2.3.1 Effect of rubber phase volume

The maximum in impact strength and ultimate elongation at intermediate rubber phase volume is an important factor in optimizing rubber efficiency. Two reasons for this are the variation in the modulus of the rubber phase and the rubber phase particle size. Previous studies have indicated that the rubber phase modulus determines the stress concentration in the matrix phase and, therefore will influence the craze formation

[Wagner & Robeson, 1970]. At constant rubber concentration as the rubber phase volume increases, the rubber phase modulus increases.

2.3.2 The effect of rubber particles size

It has been pointed out that the particle size also plays an important role in determine the fracture behavior of the polymer. Small particles are ineffective, as propagation cracks can engulf the rubber particles. Large particles size is not an efficient utility of the rubber phase, as the surface/volume ratio is diminished, thus diminishing the magnitude of craze formation [Wagner and Robeson, 1970]. Impact resistance of HIPS decreases when the average diameter of the particles becomes less than 1µm [Bucknall, 1977]. As reported in previous study, the impact strength of HIPS with particles size of 0.6-0.8µm is 48-53 J/m (nothched sample in Izod test), while the impact strength of HIPS with particles size of 1.0-3.5µm is 64-100 J/m [Soderquist *et al*., 1970]. Increasing occluded PS (rubber phase volume) increase the matrix-rubber phase surface area available for craze formation up to a point where further occlusions increase particle size and rubber phase modulus beyond their optimum level [Wagner and Robeson, 1970].

In order to study the rubber particles size on the toughening behavior, a core shell type particles has been used, which was made up from a poly (n-butyl-acrylate) (PBA) core and a PMMA outer shell [Cho *et al*.,1998]. The core shell particles were prepared from seeded emulsion polymerization. The rubbery core was slightly cross linked with 1,4-Butanediol diacrylate (BDA) in order to maintain its shape and size during melt blending with matrix PMMA. The rubber phase contents were varied from 5-20% wt. %. The impact strength increases up to a certain level of rubber phases content and decreases above that level. The blends containing 0.8µm particles clearly

show a maximum toughness around 12 wt. % of rubber phase fraction. The decrease of toughness above a certain rubber phase content is related to the decrease of the modulus and yield stress with increasing rubber phase content. If blends have a low modulus and low yield stress, the stress cannot be transferred far from the crack tip. Thus, the crack propagates without a large deformation of the matrix component near the crack tip. This results in a decrease of the stress whitening zone and the toughness. By using different test methods, the resultant toughening mechanism of rubber toughened PMMA is mainly due to multiple crazing in the three-point bending test, whereas shear yielding induced by particle cavitations is predominant in the impact test. For crazing, the molecular chains have to be disentangled during loading. Therefore, deformation can occur by crazing at the notch tip by three point bending test.

2.3.3 The effect of cross linking

From the nature of morphology of impact polystyrene, it is obvious that if the rubber was not crosslinked at all or only slightly crosslinked, the occluded polystyrene particles would be able to coalesce with the matrix during melt processing [Wagner & Robeson, 1970]. At high level of crosslinking, the modulus of the rubber phase is increased to the point that the stress concentration at the matrix rubber phase interface starts decreasing thus hindering craze formation [Wagner & Robeson, 1970]. The effect of cross linking also increases rubber phase modulus. However, over crosslinked has an adverse effect on both impact strength and ultimate elongation [Wagner & Robeson, 1970].

The morphology and properties of dynamically vulcanized elastomer/plastic blends have been extensively reported in literature. It was reported that full curing of the elastomer phase/s and the control of the cured elastomer particles diameter to 1-2μm or less, offer a significant improvement in material properties [Coran and Patel, 1980;

Sabet *et al*.,1996]. Dynamic vulcanization has been used to prepare fully cured EPDM/PP blends and found that the resultant blends can be processed as thermoplastic, although they consist of fully cured EPDM particles. This material shows some improved properties compared to those compositions consisting of partially cured elastomer particles. These include superior strength, enhanced mechanical properties, hot oil and solvent resistance, better compression set and etc. [Caron & Patel, 1980]. These results indicated a possible class of new material, which have vulcanized elastomer properties and processing characteristic of thermoplastics.

The effect of dynamic crosslinking on impact strength and other mechanical properties/ethylene-propylene-diene rubber blends has been studied [Jain *et al*., 2000]. The blends were prepared by melt mixing in a composition range of 10-40 wt % EPDM rubber. The in situ rubber curing process by using curing agent (10 wt %) and accelerator (2 wt %) based on EPDM rubber. The blends are vulcanized with RESOLE type dimethylol phenolic resin. The results showed that the crosslinking of EPDM particles have improved the tensile properties, flexural properties and impact strength of the blends. A small amount of PP/EPDM grafted copolymer is produced by the coupling of radicals, and are produced on the interface and 3-dimensional network structure during the crosslinking. The PP/EPDM grafted copolymer has strengthen the interfacial adhesion, thus improve the impact strength. As the concentration of the soft rubbery component EPDM rubber increase in the blends, the flexural strength and flexural modulus decrease. However, the vulcanized blends has higher flexural properties than the unvulcanized ones. This is due to the crosslinking effect strengthening the interfacial adhension. The size of the crosslinked structure of rubber particles is reduced due to the shear induced size reduction during vulcanization preparation. Furthermore, it also greatly inhibits the probability of the rubber cohesion

during cooling, so the number density of rubber at constant volume fraction domains is manifold with good interlocking during meltdown (i.e., enhanced molecular entanglements in and around the crosslinked structures). As soon as the stress around the crosslinked rubber particles overcome the yield stress of the matrix, the shear yielding mechanism of fracture becomes predominant over crazing and enhanced toughness is achieved.

Impact properties of dynamically vulcanized blends of nylon, styrene-acrylonitrile (SAN) copolymer and nitrile rubber (NBR) with phenolic formaldehyde (PF) compound were investigated [Wang *et al*., 2002]. The blends were prepared by melt mixing with 0-30% rubber content. The dynamically vulcanized blends with nylon/SAN ratio of 2:1 and more than 8phr PF content, showed good impact properties at ambient temperature.

The study on polypropylene/natural rubber (PP/NR) blends with blends ratio of 70/30 by adding polystyrene-modified natural rubber (SNR) as compatibiliser has been investigated [Hashim & Ong, 2002]. Melt mixing process has been used to prepared the blends with SNR content of 5 to 20 vol. %. At 5 % of SNR loading, the addition of curatives base on typical sulfur recipe (semi-efficient curative system) has improved the tensile strength and stiffeness of the blend over 20% and 40%, respectively.

The toughening mechanism of polypropylene/ ethylene-propylene-diene rubber (PP/EPDM) blends following selective cross linking by N-N'-m-phenylenebismaleimido was investigated [Ishikawa *et al*., 1996]. The blends have been prepared by melt mixing process with 5 to 30 vol. % of rubber content. The toughness of PP/EPDM blends has improved after the cross linking due to the improvement of the strength of craze is greater than the drop in the release of the constraint of strain. The effect of the cross linking of dispersed EPDM particles has increased the interfacial

adhesion and thus improve the impact strength [Inoue and Suzuki, 1995]. The impact strength of the blends is shown in Figure 2.1.
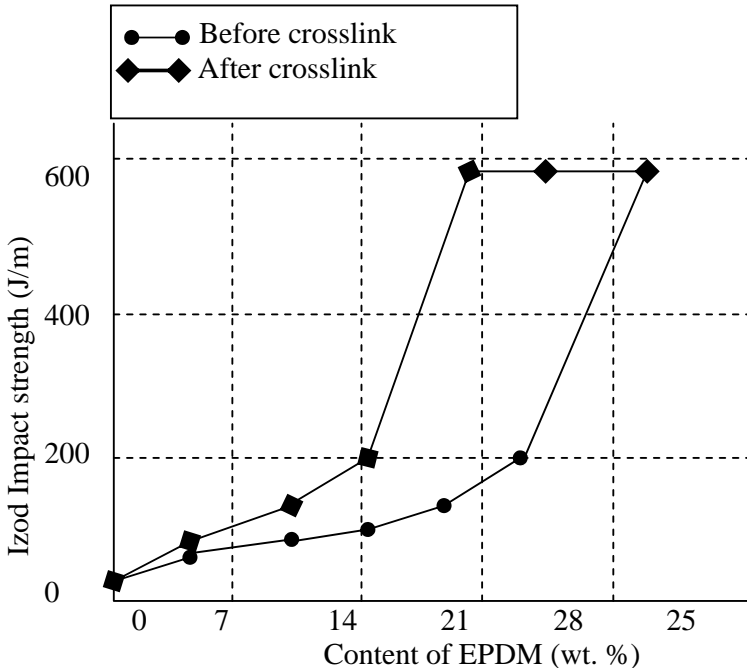

Figure 2.1: Impact strength of PP blended with EPDM following selective cross   linking in comparison with PP blends before crosslink [Inoue & Suzuki, 1995]

2.3.4 The effect of the molecular weight of matrix

The physical properties of unmodified polystyrene depend upon the weight and number average molecular weights of the polymer molecules. As reported from previous study, [Wagner and Robeson, 1970] the physical properties of matrix polystyrene are controlled by the amount of low molecular weight species present, commonly called the 'low molecular weight tail'. Low molecular weight tail, exhibited a rapid deterioration of the properties as compare to the gradual decline with addition of high molecular weight tail. Thus the low molecular weight tail has deleterious effects on the impact strength and ultimate elongation [Wagner and Robeson, 1970].

2.4 Brittle and ductile failures

Localized shear yielding and crazing are competing mechanisms for brittle fracture, although crazing is generally the more favoured precursor to brittle fracture. Both are obviously favoured by a high degree of localization of plastic strain, and hence by the polymer exhibiting strain-softening behaviour.

Figure 2.2 shows the possible interactions between shear bands and crazes. Donald and co-workers have investigated the interaction between crazes and shear bands [Kinloch & Young, 1983]. Their observations indicate that shear bands may only act as craze terminators when they grow at a craze tip and so effectively blunt the craze, e.g. region c in Figure 2.2. On the other hand, when a growing craze meets a pre-existent shear band was already formed; indeed the pre-orientation in the shear band in such as to cause premature craze breakdown and crack nucleation. Thus region b in Figure x would not, according to these workers, lead to craze termination but to premature craze breakdown and crack nucleation.

Ductile fracture involves plastic flow before failure and is usually associated with extensive shear yielding mechanism. Typical test variables which favour ductile crack growth are plane-strain, as opposed to plain-stress, conditions, elevated test temperature, relatively low rates of test and an absence of aggressive environments. It should be noted that crazing, via a multiple crazing mechanism, is also possible mechanism which may lead to ductile, tough polymers.
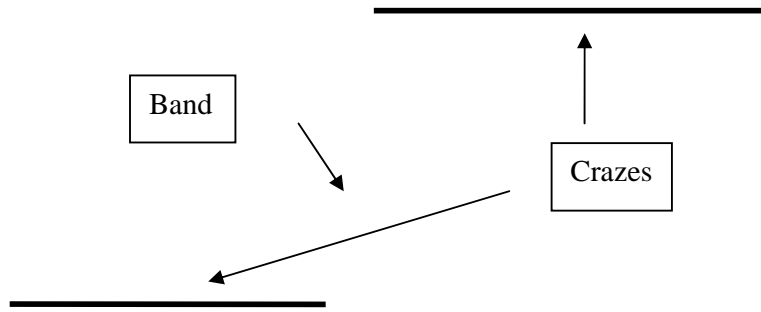
(a) Microshear band growth between craze tips
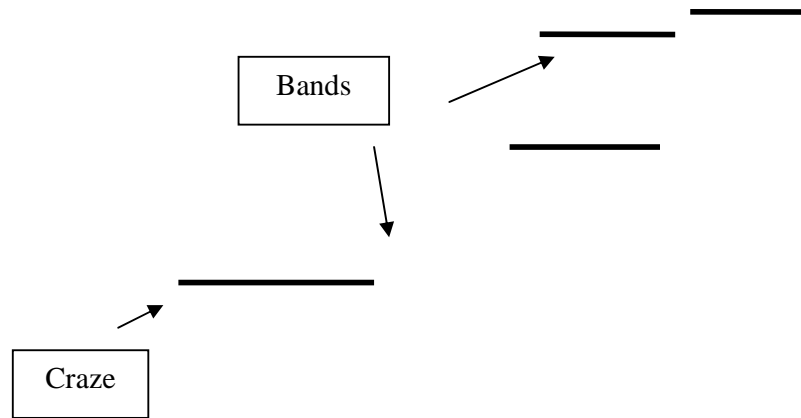
(b) Crazes terminated at pre-existing bands
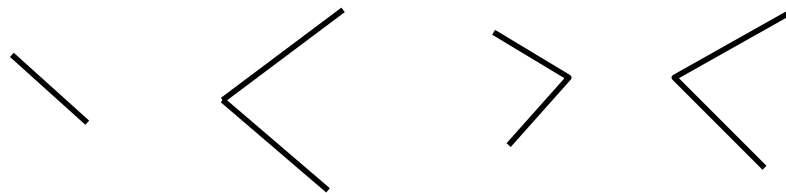
(c) Isolated crazes terminated by self-generated

Figure 2.2:   Interactions of crazes and microshear bands in PMMA and

polycarbonate [Kinloch and Young, 1983]

2.5   Compatibilization In Polymer Blends

The process of modifying interfacial properties of an immiscible polymer blend leading to the creation of polymer blend is called compatibilization [Utracki, 1990]. The achievement of the compatibilization, whether by addition of third component (compatibilizer) or by inducing in situ chemical reaction between blend components (reactive blending), has played a pertinent role in the development of polymer blend [Utracki, 1990].

Typical example for immiscible polymer blends is blend of polypropylene (PP) and polystyrene (PS) which are two of the most widely used plastics in the world [Claus J. Simpson, 1998]. PS is a brittle and amorphous polymer which belongs to the aromatic group whereas PP is a semi-crystalline and ductile polymer belongs to aliphatic group with straight carbon chains. To make both PP and PS compatible requires an intermediate substance which can bond them together while maintaining their respective properties. Commercially available material such as Styrene-Ethylene/Butadiene-Styrene copolymer (SEBS) can enhance the strain and impact strength of PP/PS blend but it causes the decreasing of certain properties such as tensile strength [Halimatuldahliana, 2002]. Wouldn't it be great to improve all properties without losing out on some along the way to create a better PP/PS blend? That is possible if a good adhesion and bond between PP and PS phase is achieved during blending with the right methodology (e.g. Temperature, rotor speed, etc) and also, with the right compatibilizer to enhance the immiscibility. This is where this work comes in handy.

The importance of polymer blending is very much significant due to its fair share of properties that is not available in a single homopolymer. These properties depend very much on the microstructure of the blends. Therefore to improve the performance, the immiscible blends usually need to undergo a compatibilization process

which modifies the interphase and/or morphology by either physical or chemical means. Compatibilization is carried out in order to achieve a reduction in the interfacial tension that facilitates dispersion of the phase, stabilization of morphology against high stress and strain processes and also enhancing the adhesion between the phases in the solid state [Cowie, 1989]. With references to Utracki [1989] and, Paul and Barlow [1980], there are a few approaches in the compatibilization of immiscible blends which are described in the sections below.

2.5.1   Addition of non-reactive Block and Graft Copolymers

Block and graft copolymers can be used as compatibilizers for polymer blends. A suitable block or graft copolymer contains a segment miscible with one blend component and another segment with the other blend component. Interfacial active graft or block copolymer of types A-B or A-C may compatibilized the immiscible polymers A and B provided that C is also miscible or capable of strong interactions with B. Significant amounts of the copolymer are expected to be located at the interface between the immiscible blend phases. The copolymer location will reduce interfacial tension between components, reducing the resistance to minor breakup during melt mixing thus reducing the size of the dispersed phase, and stabilizing the dispersion against coalescence. The finer morphology and the increased interfacial adhesion usually result in improved physical properties [Liu & Baker, 1992].

2.5.2   Addition of Reactive Block and Graft Copolymers

If polymer A and B are not capable of reacting directly with each other, they may usually be compatibilized by adding a third polymer that is capable of reacting with one or both of them. For example, addition of certain copolymer type A-C, with functional group C (where C is a long reactive functional group attached to the main chain) may compatibilized a pair of polymer A and B provided that C is chemically reactive with B [Paul & Newman, 1978c]. The non-reactive segment of the polymeric compatibilizer often has different chemical and structural identity from component A, but is still capable of imparting a certain degree of miscibility.

2.5.3   In-situ formed Copolymers

Graft or block copolymers acting as compatibilizer for polymer blends can be formed in-situ through covalent or ionic bonding during the melt blending with a polymer that has a suitable functional group. During melt blending of a pair of suitably functionalized polymer A and B, interchain block or graft copolymer may be formed at various concentrations through covalent or ionic bonding. The in-situ formed compatibilizers have certain parts or segments that are chemically reactive to those in the homopolymers and are thought to be positioned preferably at the interface. This will lower interfacial tension and promote mechanical interlocking through interpenetrations and entanglements.

Generally one component of a blend contains functional groups inherited in the polymer while the other has no intrinsic functionality. This can be done by introducing a polymer with certain functionality that is miscible so that functional group can be incorporated into the second component.