

**STUDIES ON MECHANICAL PROPERTIES OF POLY(METHYL
METHACRYLATE) AND POLY(METHYL METHACRYLATE)-MODIFIED
NATURAL RUBBER BLEND**

by

YAP GAY SUU

**Thesis submitted in fulfillment of the
requirements for the degree of
Master of Science**

Sept 2008

ACKNOWLEDGEMENT

First and foremost, I would like to thank my family for their love and support. Without their love and support, I would not have such dedication and strong enough to complete my lab work and thesis writing.

Secondly I would like to thank my supervisor, Prof. Dr. Azanam Shah Hashim. He too is blessed with infinite patience. For every chance I was given to stumble and fail as I tried to find my way, I was given two chances to find the answers and succeed. It goes without saying that his technical advice was always flawless and timed perfectly. Further thank to his dedication, guidance, advice and the generous amount of time he had spent.

And, speaking of the lab environment, I am sure that I owe most of the knowledge that I have acquired over the past two years to the technician and lab assistant, Mr Zandar, Mr Segaran, Mr Muhammad Hassan, Mr Sharul, in all the labs in Material and Mineral School. Of course not to forget all the lecturers and academic staffs that had provided their professional advice and support for the completion of this work.

Last but not least, I would like to take this opportunity to thank my colleague, Sia Choon Siong and Chin Kian Meng, because I feel that not only I have something more than just a professional relationship with them, but also for their friendship.

TABLE OF CONTENTS

	PAGE
Acknowledgement	ii
Table of Contents	iii
List of Tables	vi
List of Figures	vii
List of Abbreviations	xi
List of Symbols	xii
Abstrak	xiii
Abstract	xv
 CHAPTER 1: INTRODUCTION	
1.1 Background	1
1.2 Problem Statement	2
1.3 Objectives	4
 CHAPTER 2: LITERATURE REVIEW	
2.1 Introduction	5
2.2 Classification of Polymer Blend	6
2.3 Case Studies on Rubber-Toughened Plastics	6
2.3.1 High impact polystyrene (HIPS)	6
2.3.2 Acrylonitrile Butadiene Styrene (ABS)	9
2.4 Deproteinized Natural Rubber Latex	12
2.5 Chemical Modification of Natural Rubber	12
2.6 Properties of Poly(Methyl Methacrylate)	13
2.6.1 Toughening of PMMA	15
2.7 Strategies for Toughening	17
2.7.1 Preformed Spherical Particles	17
2.7.1.1 Core-shell Impact Modifier	19
2.7.2 Interpenetrating Polymer Networks	20
2.8 Toughening Mechanism	21
2.8.1 Energy absorption by rubber particles	22
2.8.2 Matrix crazing	22

2.8.3	Shear yielding	24
2.8.4	Cavitation and rumples	25
2.9	Modified Dynamic Vulcanization	26
2.9.1	Production of Thermoplastic Dynamic Vulcanizates	28
2.10	Factor affecting the rubber efficiency	30
2.10.1	Rubber phase content	32
2.10.2	Rubber particle size	33
2.10.3	Effect of the Type Rubber	34

CHAPTER 3: METHODOLOGY

3.1	Materials	36
3.1.1	DPNR Latex	36
3.1.2	Monomer / Polymer	36
3.1.3	Initiator	37
3.1.4	Solvent	37
3.2	Polymerization	37
3.2.1	In-situ Polymerization of MMA in DPNR Latex	38
3.3	Characterization and Analysis	39
3.3.1	Degree of Conversion	39
3.3.2	Sol-gel Analysis	40
3.3.3	Differential Scanning Calorimeter (DSC) Analysis	42
3.3.4	Scanning Electron Microscopy (SEM) Analysis	42
3.4	Compounding and Curing Behaviour	43
3.5	Blending	44
3.6	Determination of Mechanical Properties	45
3.6.1	Tensile Test	45
3.6.2	Flexural Test	46
3.6.3	Impact Test	47
3.6.4	Fracture Test	48
3.6.5	Aging Test	50
3.7	Summary of Polymerization, Sample Preparation and Testing	51

CHAPTER 4: RESULTS AND DISCUSSION

4.1	Preparation and Characterization of MNR	53
-----	---	----

4.1.1	Degree of conversion and Sol-gel Analysis	53
4.1.2	Cure characteristics and Tensile properties of MNR	57
4.2	Processing of PMMA/MNR blends	59
4.2.1	Effect of Processing Temperature	59
4.2.2	Effect of Rotor Speed	63
4.2.3	Reprocessing	65
4.3	Mechanical properties and Morphology of PMMA/MNR blends	70
4.3.1	Tensile Properties	70
4.3.2	Flexural Properties	73
4.3.3	Impact Properties	78
4.3.4	Fracture Properties	80
4.3.5	Morphology	82
	4.3.5.1 Scanning Electron Microscopy (SEM) – Fractographic Analysis	82
	4.3.5.2 Differential Scanning Calorimeter (DSC) Analysis	86
4.3.6	Aging Properties	87
4.4	Comparison with other studies	91
4.4.1	Comparison of PMMA/MNR with PBA-based PMMA blend	91
4.4.2	Comparison of PMMA/MNR with self-reinforcing PMMA	94
CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH		
5.1	Conclusions	100
5.2	Recommendation for Future Research	101
REFERENCES		102

LIST OF TABLES

		PAGE
Table 2.1	Properties of PMMA	14
Table 2.2	Advantages and Disadvantages of PMMA	15
Table 3.1	Specifications of DPNR lattices	36
Table 3.2	Recipe and reaction parameters of in-situ emulsion polymerization of MMA in DPNR latex.	38
Table 3.3	Recipes for the compounding of MNR	43
Table 4.1	Degree of conversion and sol-gel analysis results	56
Table 4.2	Cure characteristic and tensile properties of MNR cured with different recipe	57
Table 4.3	Glass transition temperature, T_g , for pure PMMA and PMMA/MNR blends with different MNR content	87
Table 4.4	Properties retention for pure PMMA and PMMA/MNR blends with curatives	90

LIST OF FIGURES

		PAGE
Figure 2.1	Schematic representation of core-shell modifiers; (a) 2 layered core-shell particle and (b) 3 layered core shell particle	18
Figure 2.2	Characteristic change in mixing torque and temperature during dynamic curing of a thermoplastic/rubber blend [Binet-Szulman, 1993]	29
Figure 2.3	The optimum rubber particle diameter, d , vs entanglement density, ν_e , of brittle matrices based on notched Izod impact strength [Wu, 1990]	33
Figure 3.1	Reactor for the polymerization	37
Figure 3.2	Apparatus setup for sol-gel analysis	41
Figure 3.3	Schematic representation of Thermo HAAKE Polydrive	45
Figure 3.4	Summary of research methodology	52
Figure 4.1	Diagram of PMMA modified NR and free PMMA homo-polymer	53
Figure 4.2	Conversion-time curves of in-situ emulsion polymerization of MMA in DPNR latex	54
Figure 4.3	Stress-strain curve of uncured and curing with different recipe of MNR	58
Figure 4.4	Torque-time curves of blends with 5% MNR content (wt %) sheared at 60 rpm rotor speed at different temperatures	60
Figure 4.5	Tensile strength of blends with 5% MNR content (wt %) sheared at 60 rpm rotor speed at different temperatures	61
Figure 4.6	Young's modulus of blends with 5% MNR content (wt %) sheared at 60 rpm rotor speed at different temperatures	61
Figure 4.7	Elongation at break of blends with 5% MNR content (wt %) sheared at 60 rpm rotor speed at different temperatures	62
Figure 4.8	Torque-time curves of blends with 5% MNR content (wt %) sheared at different rotor speed at 200°C	63

Figure 4.9	Tensile strength of blends with 5% MNR content (wt %) sheared at different rotor speed at 200°C	64
Figure 4.10	Young's modulus of blends with 5% MNR content (wt %) sheared at different rotor speed at 200°C	64
Figure 4.11	Elongation at break of blends with 5% MNR content (wt %) sheared at different rotor speed at 200°C	65
Figure 4.12	Tensile strength and Elongation at break of blends with 5% MNR content (wt %) sheared at 50 rpm rotor speed at 200°C	66
Figure 4.13	Tensile strength of blends with 5% MNR content (wt %) sheared at both 170°C and 200°C at 50 rpm rotor speed	67
Figure 4.14	Young's modulus of blends with 5% MNR content (wt %) sheared at both 170°C and 200°C at 50 rpm rotor speed	68
Figure 4.15	Elongation at break of blends with 5% MNR content (wt %) sheared at both 170°C and 200°C at 50 rpm rotor speed	69
Figure 4.16	Tensile strength of pure PMMA, PMMA/MNR blends with curative and without curative	70
Figure 4.17	Young's Modulus of pure PMMA and PMMA/MNR blends with curative and without curative	71
Figure 4.18	Elongation at break of pure PMMA and PMMA/MNR blends with curative and without curative	72
Figure 4.19	Load-displacement curves in flexural test of pure PMMA and PMMA/MNR blends	74
Figure 4.20	Flexural strength of pure PMMA and PMMA/MNR blends	74
Figure 4.21	Flexural modulus of pure PMMA and PMMA/MNR blends	75
Figure 4.22	Flexural strain of pure PMMA and PMMA/MNR blends	76
Figure 4.23	The trend of elastic energy at critical stage (U_c) or elastic energy at yield point (U_y) as a function of MNR content of PMMA/MNR blends	77

Figure 4.24	Impact strength of unnotched and notched samples of pure PMMA and PMMA/MNR blends	78
Figure 4.25	Impact strength increment (%) of notched and unnotched samples of pure PMMA and PMMA/MNR blends	79
Figure 4.26	Load-displacement curves in flexural test of pure PMMA and PMMA/MNR blends	81
Figure 4.27	Plane-strain fracture toughness, K_{IC} and critical strain release energy, G_{IC} of pure PMMA and PMMA/MNR blends	82
Figure 4.28	SEM micrograph of fracture surface at room temperature of pure PMMA (1000x)	83
Figure 4.29	SEM micrograph of fracture surface at room temperature of PMMA/MNR blends with (a) 2.5%, (b) 5.0%, (c) 7.5% and (d) 10.0% MNR content (wt %) (1000x)	84-86
Figure 4.30	Heat flow vs temperature for pure PMMA and PMMA/MNR blends with different MNR content (wt %)	86
Figure 4.31	Tensile strength for aging test of pure PMMA and PMMA/MNR blends with curatives	88
Figure 4.32	Young's Modulus for aging test of pure PMMA and PMMA/MNR blends with curatives	89
Figure 4.33	Elongation at break for aging test of pure PMMA and PMMA/MNR blends with curatives	89
Figure 4.34	Tensile strength of pure PMMA, PMMA/MNR blends and PBA-based PMMA blend	92
Figure 4.35	Young's Modulus of pure PMMA, PMMA/MNR blends and PBA-based PMMA blend	92
Figure 4.36	Elongation at break of pure PMMA, PMMA/MNR blends and PBA-based PMMA blend	93
Figure 4.37	Plane-strain fracture toughness, K_{IC} of pure PMMA, PMMA/MNR blends and PBA-based PMMA blend	93
Figure 4.38	Tensile strength of pure PMMA, PMMA/MNR blends and self-reinforcing PMMA	95
Figure 4.39	Young's Modulus of pure PMMA, PMMA/MNR blends and self-reinforcing PMMA	96

Figure 4.40	Elongation at break of pure PMMA, PMMA/MNR blends and self-reinforcing PMMA	96
Figure 4.41	Flexural strength of pure PMMA, PMMA/MNR blends and self-reinforcing PMMA	97
Figure 4.42	Flexural modulus of pure PMMA, PMMA/MNR blends and self-reinforcing PMMA	98
Figure 4.43	Plane-strain fracture toughness, K_{IC} of pure PMMA, PMMA/MNR blends and self-reinforcing PMMA	98

LIST OF ABBREVIATIONS

ABS	– acrylonitrile butadiene styrene
ASTM	– American Society for Testing and Materials
CIIR	– chlorinated butyl rubber
DSC	– differential scanning calorimetry
DPNR	– deproteinized natural rubber
EA TPV	– elastomer alloy thermoplastic vulcanizates
EB	– elongation at break
EPDM	– ethylene propylene diene monomer
EV	– efficient vulcanization
EVA	– ethylene-vinylacetate copolymers
HDPNR	– highly deproteinized natural rubber
HIPS	– high impact polystyrene
IPN	– interpenetrating polymer networks
iPP	– high impact isotactic polypropylene
IPPD	– N-isopropyl-N'-phenylparaphenylenediamine
LDPE	– low-density polyethylenes
MBTS	– dibenzo thiazolyl disulphide
MMA	– methyl methacrylate
MNR	– poly(methyl methacrylate)-modified natural rubber
NR	– natural rubber
PA6	– polyamide 6
PBA	– poly(butyl acrylate)
PE	– polyethylenes
PMMA	– poly(methyl methacrylate)
PS	– polystyrene
PVC	– poly(vinyl chloride)
rpm	– rotation per minute
RT-PMMA	– rubber-toughened PMMA
SAN	– styrene copolymer with acrylonitrile
SBR	– styrene butadiene rubber
SEM	– scanning electron microscopy
SENB	– single-edge notch bending
SNR	– polystyrene-modified natural rubber
SRC-PMMA	– self-reinforced composite poly(methyl methacrylate)
TDV	– thermoplastic dynamic vulcanizates
TEM	– transmission electron microscopy
THF	– tetrahydrofuran
TMTD	– tetramethyl thiuram disulfide
TPEs	– thermoplastic elastomers
wt	– weight
ZnO	– zinc oxide

LIST OF SYMBOLS

T_g	–	glass transition temperature
R	–	particle radius
T_{BT}	–	brittle-to-tough transition temperature
ν_e	–	entanglement density
d	–	particle diameter
C_∞	–	characteristic ratio of the chain
G_R	–	shear moduli of the rubber
G_M	–	shear moduli of the matrix
Z	–	strain rate
L	–	support span
d	–	depth of beam
σ_f	–	flexural stress
P	–	load at given point on the load deflection curve
b	–	width of beam
R	–	crosshead speed
K_{IC}	–	Plane-strain fracture toughness
P_Q	–	maximum load
S	–	beam span
B	–	specimen thickness (depth)
W	–	specimen width
a	–	crack length
G_{IC}	–	critical strain energy release rate
ν	–	poisson ratio
E	–	Young's modulus
M_a	–	value of tensile strength / properties after aging
M_b	–	value of tensile strength / properties before aging
t_{90}	–	specimen depth (width)
U_c	–	elastic energy at critical stage
U_y	–	elastic energy at yield point
σ_c	–	critical stress
σ_y	–	yield stress
E_f	–	flexural modulus
K_c	–	fracture toughness
σ	–	maximum stress
a	–	length of the crack for edge cracks
G_I	–	strain energy release rate
K_I	–	stress intensity factor

**KAJIAN KE ATAS SIFAT MEKANIKAL ADUNAN POLI(METIL
METAKRILAT) DAN GETAH ASLI TERUBAHSUAI POLI(METIL
METAKRILAT)**

ABSTRAK

Thesis ini menyelidik aspek parameter yang terlibat semasa pengadunan polimer (pencampuran lebur) poli(metal metakrilat) (PMMA) dengan getah asli terubahsuai PMMA (MNR). Keberkesanan MNR sebagai penguat bagi PMMA dikaji berdasarkan sifat mekanikal akhir dan morfologi adunan PMMA/MNR. MNR dihasilkan di dalam makmal melalui pemolimeran in-situ monomer MMA di dalam lateks getah asli ternyahprotein.

Sifat-sifat pematangan MNR sebagai getah terubahsuai dikaji menggunakan sistem pemvulkanan cekap (EV), pemvulkanan separa-cekap (semi-EV) dan pemvulkanan tanpa sulfur. Berdasarkan kajian tersebut, system semi-EV memberikan sifat tegangan yang optimum. Dengan mengaplikasikan prinsip pemvulkanan dinamik, MNR tersebut disebatikan dengan resepi sistem pemvulkanan separa-cekap dan sebatian yang terhasil diadunkan dengan resin PMMA komersil menggunakan Thermo HAAKE Polydrive. Kesan beberapa parameter seperti kelajuan rotor, suhu, masa pericihan dan pecahan berat fasa getah yang tersebar semasa pencampuran lebur telah dikaji. Sifat tegangan yang optimum diperolehi pada 200°C dengan kelajuan rotor 50 putaran seminit. Tetapi, disebabkan masa pericihan yang terhad, adunan tersebut diproses semula untuk mendapatkan penyebaran dan penaburan zarah getah yang lebih baik. Keputusan menunjukkan,

berdasarkan 5% berat pembebanan MNR, syarat pemrosesan yang terbaik adalah, pra-adun PMMA dan MNR selama 5 minit (4 minit pra-ricih PMMA + 1 minit selepas MNR ditambahkan) pada 170°C dengan kelajuan rotor 50 putaran seminit dan diikuti adunan PMMA/MNR diadun semula selama 4 minit pada 200°C dengan kelajuan rotor 50 putaran seminit.

Adunan PMMA/MNR, dengan kuratif yang terkandung di dalam komponen MNR, dikaji pada pembebanan 2.5, 5.0, 7.5 dan 10.0 % berat MNR. Sifat mekanikal dan morfologi adunan PMMA/MNR dikaji melalui ujian tegangan, lenturan, hentaman (bertakuk dan tidak bertakuk), bengkokan takuk tepi tunggal (SEN-B), analisis SEM dan DSC. Sifat tegangan dan lenturan yang optimum diperolehi pada 2.5% pembebanan MNR manakala pada 7.5% pembebanan MNR, sifat hentaman dan kekuatan raka yang optimum diperolehi. Apabila dibandingkan dengan PMMA tulen, kekuatan tegangan dan pemanjangan pada pemutusan meningkat sebanyak 17% dan 41% masing-masing, manakala kekuatan lenturan dan terikan lenturan meningkat sebanyak 12% dan 72% masing-masing pada 2.5% pembebanan MNR. Secara konsisten, keserasian MNR yang lebih baik pada 2.5% diperhatikan melalui kajian morfologi di mana tiada kavitasi diperhatikan pada permukaan rekah. Bagi keputusan hentaman, peningkatan sebanyak 43% dan 20% diperhatikan pada 7.5% pembebanan MNR bagi sampel tidak bertakuk dan bertakuk apabila dibandingkan dengan PMMA tulen. Bagi kekuatan raka, K_{IC} and G_{IC} meningkat sebanyak 81% and 412% masing-masing pada 7.5% pembebanan MNR apabila dibandingkan dengan PMMA tulen.

**STUDIES ON MECHANICAL PROPERTIES OF POLY(METHYL
METHACRYLATE) AND POLY(METHYL METHACRYLATE)-MODIFIED
NATURAL RUBBER BLEND**

ABSTRACT

This study investigated aspects of parameters involved during the blending (melt-mixing) of poly(methyl methacrylate) (PMMA) with PMMA-modified natural rubber (MNR). The effectiveness of the MNR as a toughener for PMMA was also assessed based on the final mechanical properties and morphology of the PMMA/MNR blends. MNR was first prepared in the laboratory by *in situ* polymerization of MMA monomer in deproteinized natural rubber latex.

The cure characteristics of MNR as a modified rubber were investigated using efficient vulcanization (EV), semi efficient vulcanization (semi-EV) and sulfurless vulcanization systems. Based on the investigation, semi-EV system gave the optimum tensile properties. By applying the principle of dynamic vulcanization, the MNR was first compounded with semi-EV recipe and the resultant compound was blended with commercial PMMA resin using Thermo HAAKE Polydrive. The effect of several parameters such as rotor speed, temperature, shearing time and weight fraction of the dispersed rubber phase during melt-mixing was studied. The optimum tensile properties were obtained at 200°C with 50 rpm rotor speed. However, due to constraint shearing time, the blends were reprocessed to obtain better dispersion and distribution of rubber particles. The results showed that the best processing conditions, based on 5 wt% of MNR loading, were pre-blending of PMMA and MNR for 5 minutes (4 minutes pre-shearing PMMA + 1 minute after

MNR addition) at 170°C and 50 rpm followed by blending the PMMA/MNR blend again for 4 minutes at 200°C and 50 rpm.

PMMA/MNR blends, with curatives contained in the MNR component, were studied at 2.5, 5.0, 7.5 and 10.0 wt % MNR loading. The mechanical properties and morphology of the PMMA/MNR blends were studied through tensile, flexural, impact (notch and unnotched) properties, single-edge notch bending (SEN-B), SEM and DSC analysis. The optimum tensile and flexural properties was obtained at 2.5% MNR loading while at 7.5% MNR loading, optimum impact and fracture toughness was obtained. When compared with pure PMMA, the tensile strength and elongation at break increased about 17% and 41% respectively, while the flexural strength and flexural strain increased about 12% and 72% respectively at 2.5% MNR loading. Consistently, better compatibility of MNR at 2.5% was observed through morphological studies where no cavitations were observed on the surface of the fractured surface. For the impact results, increment of 43% and 20% were observed at 7.5% MNR loading for the unnotched and notched samples when compared to pure PMMA. For the fracture toughness, the K_{IC} and G_{IC} increased about 81% and 412% respectively at 7.5% MNR loading when compared with pure PMMA.

CHAPTER 1: INTRODUCTION

1.1 Background

The incorporation of elastomeric particles into the bulk of thermoplastics brittle polymers is a well known technique used to improve the toughness of the plastics. Toughness can be defined as the amount of energy that a material can absorb before breaking. The technique is applied on the commercial high impact polystyrene (HIPS), where the polystyrene is blended with rubbers like polybutadiene or copolymers with styrene. Besides polystyrene, similar blends with poly(methyl methacrylate) are also reported [Flavio *et. al.*, 1996, V. Neliappan *et. al.*, 1997]. However, these blends are in principle incompatible and immiscible, which would lead to the present of a significant phase separation phenomena (without any interactions between phases), resulting in poor properties of the final product. Since these immiscible blends are thermodynamically unstable, they must be stabilized to prevent coalescence during melt processing [Utracki, 1989]. This process of stabilizing polymer blends is commonly called compatibilization. A compatibilization strategy which is frequently proposed is the addition of a premade block copolymer composed of blocks that are each miscible with one of the homopolymers. Theory suggests that block copolymers will prefer to extend across the interface [Deanin & Manion, 1999].

Most experimental studies have been carried out by casting from solution [Ong, 2001, Neoh, 2003, Van, 1999]; however, commercially, blends are prepared by melt mixing. Furthermore, it appears that all commercial blends made from highly immiscible polymers are compatibilized reactively. That is, a block or graft

copolymer is formed by coupling of reactive groups on each of the immiscible polymers. There are several problems in compatibilizing multiphase structures with block copolymer in the melt. The viscosity of block copolymers are high and thus may be difficult to disperse. These copolymers are typically expensive so it is desirable to minimize their concentration.

1.2 Problem Statement

PMMA is a commodity plastic with excellent optical clarity, good weathering resistant, high tensile strength and tensile modulus. However, due to its brittle nature, its application is quite limited. Thus, by increasing its toughness while maintaining most of its other properties, the application field for PMMA can be widen. On the other hand, natural rubber is a low cost material which is easily available. It has poor weather resistance but this is easily solved by adding of curative ingredients into it. It has low modulus but high tensile elongation. Blending of elastomer with thermoplastic is a common way of producing a material with high impact properties. The impact properties refer to the abilities of materials to absorb energy when subjected to shock loading before fracture. Thus, by introducing elastomeric particles into thermoplastics, the amount of energy absorb by material before breaking will be increased. However, theoretically, a better blend can be produced by dynamic vulcanization [József, 1999]. The principle of dynamic vulcanization is by *in-situ* curing or cross-linking of the rubber component of thermoplastic and elastomer blend via an intensive or kneading process. Conventionally, the curatives are usually added during the melt mixing process.

However, for this research, a modified dynamic vulcanization was used. MNR was separately compounded with curatives by using a two-roll mill and the resultant MNR compound was added into PMMA during melt mixing. Based on a previous study [Ong, 2001], a conventional dynamic vulcanization was found to be less effective due to the limitation of the shear rate and also that the curatives tend to be dispersed in both the thermoplastic and elastomer components. The limitation of the shearing rate leads to a poor dispersion of the curatives, while the dispersion of curatives in the thermoplastic causes the curing system to be less effective.

In this research, pure PMMA was blended with MNR. Since the main purpose was to evaluate the effectiveness of the MNR as a toughener, the PMMA-MNR blends were limited to PMMA-dominant blends. The MNR was first prepared in the laboratory by *in situ* polymerization of methyl methacrylate in deproteinized natural rubber latex. The MNR prepared was expected to have a high degree of grafting i.e. high amount of PMMA in the MNR is chemically bonded onto the natural rubber backbones. It was proven that by using highly deproteinized natural rubber latex, high degree of grafting can be obtained [Nguven, 1999, Ragvinder, 2000, Ong, 2001]. Because of this high degree of grafting, there would be a high degree of adhesion/interaction between phases, in this case between the PMMA matrix and PMMA component of the MNR and this would contribute to stability against segregation during processing [Paul, 1978]. Thus, a high degree of grafting is essential to ensure a good stress transfer between phases.

From this research, it is expected that a good compatibility between PMMA and MNR can be observed. This is because MNR contained grafted PMMA chains

which are the same as the matrix used. Subsequently, a better interfacial interaction is expected which would provide better stress transfer. As a result, the impact resistance and toughness of PMMA/MNR blends at some amount of MNR loading should be significantly improved when compared to pure PMMA.

1.3 Objectives

The objectives of this research are:

1. To prepare MNR and to determine its degree of grafting, cure characteristics and tensile properties
2. To evaluate and decide the best or most suitable processing conditions for producing PMMA - MNR natural rubber blends.
3. To study the effect of MNR as a toughener for PMMA using the principles of dynamic vulcanization via tensile, flexural, and impact properties and morphological observations

CHAPTER 2: LITERATURE SURVEY

2.1 Introduction

Polymer blends are a key component of current polymer research and technology. This is due to their ease of production of new materials by mixing and achieving the much needed final properties for applications. However, an increasing set of characterization techniques have also led to an increased understanding of the toughening mechanisms involved in polymers mixing, their fundamental interactions, and how these interactions affect their final properties through different mode of deformations. This understanding is however becoming a challenge for both scientific and industrial viewpoints, due to the increasing economical impact of polymer blends and alloys in many domains affecting our everyday life.

The definition of polymer blends is two or more polymer chains having constitutionally or configurationally differing features in intimate combination but not bonded to each other [composite.about.com]. The combination can be either physical blends or chemical blends in which the polymers are covalently bonded, example copolymers.

The most widespread examples of polymer blends involve modification of impact toughness by incorporation of rubber into brittle polymer matrix. Most commercial blends consist of two polymers combined with small amounts of a third, compatibilizing polymer typically a block or graft copolymer [Cavanaugh *et. al.*, 1996]. Polymer blending can be made using a variety of methods; such as phase separation and preformed particles, melt compounding and reactive technologies

such as precipitation polymerization and reactive extrusion [Brown & Orlando, 1988]. Polymer blends can be easier to process than a single polymer with similar properties. The possible blends from a given set of polymers offer better physical properties than do the individual polymers.

2.2 Classification of Polymer Blend

Polymer blends can be classified into three main categories, a) rubber-rubber blends, b) plastic-rubber blends and c) plastic-plastic blends. This research is focus on plastic-rubber blends where it can be further divided into rubber-toughened plastics which are more for impact applications and thermoplastic elastomers (TPEs) which can be processed like a thermoplastic but properties wise behave more like elastomers. Rubber-toughened plastics usually contain 5-20% rubbers which are dispersed in the matrix [Bucknall, 1978].

2.3 Case Studies on Rubber-Toughened Plastics

The simplest way to rubber toughened materials is to melt blend a rubber with matrix polymer to be toughened. This approach, however, often produces relatively poor materials due to the difficulty in controlling the size and morphology of the rubbery domains and interface between rubber and matrix polymer.

2.3.1 High impact polystyrene (HIPS)

High impact polystyrenes (HIPS) are considered to be styrene polymers modified by the incorporation of a rubber component. As indicated by their name, high impact polystyrene are characterized by greatly increased impact strength (40 to 80 kJm^{-2} or more) compared with unmodified standard polystyrene (about 20 kJm^{-2}),

reflecting the influence of the micro-phase structure of the modified polymer. In common grades, the content of modifying rubber usually varies around 5%, but can be even greater for special grades [www.bayplastics.co.uk].

Basically there are two conventional ways to produce high-impact polystyrene. The impact strength of polystyrene is modified by the incorporation of a rubber component and can be manufactured on an industrial scale either by mechanical blending of the two components under controlled conditions or by grafting of the polymerizing styrene onto the rubber, usually by bulk (mass) or suspension polymerization. HIPS produced by mechanical blending with the rubber is based on the styrene homopolymer, which must be prepared by the normal polymerization procedures. Selection of the modifying rubber is always a compromise, but at least partial compatibility with the polystyrene phase is a necessary condition for achieving adequate impact strength. The actual process of blending the two components in the melt can be carried out using various types of apparatus, such as batch or continuous kneaders of various designs, heated two-roll mills, twin-screw extruders, etc. During mechanical blending, the kneaded mixture is exposed to considerable shear stress at a temperature of about 200°C, leading to dispersion of the rubber component in the form of irregular particles (with an optimal size of about 2 to 5µm) in the continuous polystyrene phase. Simultaneously, the mechano-chemically generated macroradicals give rise to cross-linking of the rubber phase and, to a certain degree, also to the formation of chemical bonds between the two phases (grafting). The homogeneity of the product depends on the efficiency of the blending process. Mechanical blending can also be used for the preparation of

polyblends such as styrene plastics with polyphenylene oxide or ABS polymer with polycarbonate.

Another method for preparing HIPS is by grafting of the polymerizing styrene onto the rubber. Polymerization of styrene monomer containing dissolved polybutadiene yields both the styrene homopolymer and the grafted copolymer, polybutadiene-graft-polystyrene, where polystyrene side chains are grafted onto the main chain of polybutadiene. In the initial stages, preparation of the polybutadiene solution and prepolymerization, are practically identical for both processes. Butadiene rubber in small pieces is first dissolved in styrene and dissolution is accelerated by stirring and increasing temperature to 70°C. The homogenized polybutadiene solution is then fed into a reactor in which prepolymerization is carried out. The process can be initiated by elevated temperature or in the presence of a suitable initiator. Continuous stirring is conducted to remove heat of polymerization. As conversion reach 2 – 3%, the originally transparent solution becomes turbid as phase separation occurs due to the incompatibility of polystyrene and polybutadiene [White & Patel, 1975]. The system forms an emulsion in which the dispersed phase, with small volume, is a solution of polystyrene in styrene and the continuous phase is a solution of polybutadiene in styrene [Molau, 1965]. The grafted copolymer is concentrated at the interface and act as an emulsifier. As polymerization continued, the volume ratio of the two phases changes – the volume of the polystyrene increase and polybutadiene decrease. At 8 – 14% conversion, the system reaches a point where volume of the solution of polystyrene in styrene became too large to be dispersed phase and vice versa. At this stage of polymerization, phase inversion occurs in a relatively narrow concentration intervals.

However, phase inversion only occurs under sufficiently strong shearing agitation. The final product would consist of continuous phase (matrix) of cross-linked polybutadiene with dispersed polystyrene particles.

2.3.2 Acrylonitrile Butadiene Styrene (ABS)

Industrially important Acrylonitrile Butadiene Styrene (ABS) polymers are two-phase polymer systems. A modifying rubber (usually polybutadiene or the butadiene copolymer with styrene or acrylonitrile) is dispersed as small discrete particles throughout the continuous phase (matrix) of a styrene copolymer with acrylonitrile (SAN), where part of the SAN copolymer is grafted onto the rubber particles. Thus the ABS copolymer is rubber-modified SAN copolymer, just as high-impact polystyrene is rubber-modified polystyrene. The fraction of rubber component in ABS polymers is usually greater than in high-impact polystyrenes. This value varies from 10-25% for common commercial grades and special grades (e.g. for blending with polyvinyl chloride) can even contain over 45% rubber. The higher rubber content and the different type of polymer forming the continuous phase result in the ABS polymers having a number of properties better than common grades of high-impact polystyrene. Thus, ABS polymers occupy an intermediate position between inexpensive, mass-produced commodity plastics (standard polystyrene, polypropylene, etc) and the much more expensive engineering plastics (polycarbonates, polyacetals, etc.), that are used for engineering and other high-performance applications.

ABS polymers can be prepared by mechanical blending of the individual components or by grafted polymerization of a mixture of styrene with acrylonitrile in

the presence of a suitable rubber component. One of the strategies to the modification of toughness of SAN copolymer is through mechanical blending with rubber [Basdekis, 1964]. The copolymer of butadiene with acrylonitrile was usually used as the rubber component to obtain adequate compatibility. However, after thorough blending of rubber in the homogeneous blends, it acts as a plasticizer of the SAN copolymer with only a small increase in the impact strength. Optimal dispersion of the rubber particles can be achieved only with sufficiently cross-linked rubber containing 30 to 50% gel (for example, prepared by copolymerization with a small amount of divinyl benzene). Blending of the two components in an optimum ratio (for example, 65 parts by weight of SAN copolymer, 34 parts nitrile rubber and 1 part other additives) is carried out as for high-impact polystyrene. The blend is processed on the mill roll at a temperature of 150 to 250°C or in a Banbury mixer at a temperature of up to 235°C.

For blending in latex form, both the component copolymers can readily be prepared by emulsion polymerization, and it is sometimes advantageous to blend them in the latex stage. SAN copolymer latex and butadiene-acrylonitrile latex are fed in a suitable ratio from the storage tanks into the blending tank; an antioxidant emulsion is also added simultaneously. After complete mixing, the latex mixture is coagulated using an electrolyte solution and the crumbs obtained are washed and dried. Once again, optimal properties can be obtained only with mechanical processing of the blend [Basdekis, 1964] (in internal mixers, special extruders, etc.) Simultaneously, additives are also incorporated into the polymers in this stage, such as lubricants, colourants, additional antioxidants, etc. The greatest drawback of ABS polymers prepared by mechanical blending is their decreased impact strength at low

temperatures. In addition, processing is difficult and injection moulded products have poor surface properties. These disadvantages are eliminated for grafted types, which have almost completely replaced blended types. However, the blending principle is sometimes also used at certain stages in the preparation of ABS polymers.

Another type of preparation method for ABS polymer is by grafting. Grafting in emulsion polymerization remains the most widely used method for the production of ABS polymers, even though emulsion technology is more complicated than other procedures. Its advantages lie in its ability to yield a wide variety of products and the rapid conversion of one grade to another. Most grades of ABS polymers for injection moulding applications are produced by emulsion technology.

This process is practised industrially in a great many forms. The oldest procedures carry out grafting of the polybutadiene separately from the preparation of the SAN polymer. In the usual procedure, polybutadiene latex containing 30 to 60% polybutadiene is first prepared by emulsion polymerization. After addition of a short-stopping agent, removal of residual unpolymerized monomer and filtration of the latex, a mixture of styrene and acrylonitrile monomers, a further emulsifier and a molecular weight modifier (such as tert. dodecanethiol) are added. The mixture is stirred at 50°C to permit adsorption of the monomer by the latex particles. Polymerization is initiated by addition of a water-soluble initiator (peroxydisulphate or any one of a number of redox systems) and proceeds at a temperature of about 80°C; it is controlled so that most of the monomers are grafted onto the polybutadiene particles. The latex of the grafted polymer, with relatively high polybutadiene content, is then blended in the required ratio with the separately

prepared SAN copolymer latex. At this stage, the procedure is completely analogous to that employed in the preparation of ABS polymers by mechanical blending of the latexes. However, the grafted polymer can also be isolated by coagulation in the form of crumbs and dried and blended with the SAN copolymer in a plastic state. It is then also possible to employ SAN copolymer prepared by suspension, mass or solution polymerization. The described alternative is thus a combination of grafting and blending. Separate preparation of the components permits better control of their composition and structure and thus also of the final ABS polymer properties [Bley & Mohammad, 1983]. It is also possible to prepare the final product directly in a single step by grafting in emulsion [Calvert, 1966]. A mixture of styrene and acrylonitrile monomers is then added to the polybutadiene latex, either all at once at the beginning of the polymerization or gradually in several batches. The final latex of the ABS polymer contains both the grafted and free SAN copolymer.

2.4 Deproteinized Natural Rubber Latex

Deproteinised Natural Rubber (DPNR) is a purified form of natural rubber (NR) from which most of the ash and protein components have been removed. It contains about 96% rubber hydrocarbons compared to about 93% for normal natural rubber grades. The removal of these non-rubber components confers special attributes to the rubber which enhance its value in certain specialized applications.

2.5 Chemical Modification of Natural Rubber

There are a lot of researches been done on chemical modification of Natural Rubber (NR) since 1920s. The purpose of chemical modification on NR is to improve NR properties because NR some inferior properties such as poor ageing

resistance, poor oil resistance, poor wet grip and etc, even though NR also has good properties such as high strain, high tensile strength, high resilience, good water resistance and etc. NR is a very reactive polymer because of its special structure. The presence of an olefinic C=C double bond and 7 allylic hydrogen atoms make the rubber very reactive [Gelling & Porter, 1988]. The chemical modification of NR can be carried out in latex, solution or dry phase [Allen, 1963]. The purpose of the chemical modification of natural rubber is to improve the physical properties of NR such as oil resistance, hardness, wet skid resistance, ageing resistance etc.

Some of the important chemically modified NR have been discovered and are in still use today such as: cyclized natural rubber, chlorinated natural rubber, hydrochloride natural rubber, poly(methyl methacrylate) – modified NR (Heveaplus MG), and epoxidized NR (ENR).

2.6 Properties of Poly(Methyl Methacrylate)

The properties that make PMMA a highly-prized plastic are its good mechanical strength, its outstanding optical properties (clarity, brilliance, transparency), and its extremely good weather resistance. It is classified as a hard, rigid, but brittle material. This favorable profile can be supplemented by the surface modification of semi-finished products (e.g., scratch-resistant or antistatic coating), coloring or pigmentation, and treatment with flame retardants to open up a wide variety of potential uses for this polymer. The most important physical properties of PMMA are summarized in Table 2.1; a distinction is made between cast PMMA ($M_w > 10^6$) and PMMA extruded from molding compounds ($M_w < 5 \times 10^5$).

Table 2.1: Properties of PMMA

Physical properties of PMMA (standard values at 23°C and 50% R.H. for Plexiglas GS 233 and Plexiglas XT 7H)	
Property	Cast (extruded)*
Density, g/cm ³	1.18
Charpy impact strength, kJ/m ²	15
Izod-test value, kJ/m ²	1.6
Tensile strength (1/1 test bar 3, v = 5 mm/min), MPa	80 (72)
Elongation at break (1/1 test bar 3, v = 5 mm/min), %	5.5 (4.5)
Flexural strength (standard bar 80x10x4 mm), MPa	115 (105)
Long term tensile strength (1/1 test bar, t = 10 000 h), MPa	38 (30)
Modulus of elasticity (short-term value), MPa	3300
Shear modulus (ca. 10 Hz), MPa	1700
Ball indentation hardness $H_{961/30}$, MPa	200 (190)
Degree of transmission (3 mm thickness, illumination D65, visible region, $\lambda = 380-780$ nm), %	92
Refractive index n_D^{20}	1.491
Linear thermal expansion coefficient (0–50°C), K ⁻¹	70×10^{-6}
Shrinkage onset temperature, °C	> 80
Vicat softening point (method B), °C	115 (102)
Heat distortion temperature (at flexural stress of 1.8 MPa), °C	105 (90)

Table 2.2: Advantages and Disadvantages of PMMA

Advantages	Disadvantages
<ul style="list-style-type: none"> • high mechanical strength and hardness • high rigidity • excellent transparency • easy to polish • good thermal stability • good insulation properties • low water absorption • excellent weather resistance 	<ul style="list-style-type: none"> • possible stress problems • low chemical resistance • low impact resistance • brittle

2.6.1 Toughening of PMMA

Poly(methyl methacrylate) (PMMA), is one of the more brittle amorphous thermoplastic materials. It has glass transition temperature T_g of about 100°C. In the glassy state the molecular mobility is low and the polymer chains are not able to undergo large-scale molecular motions in response to rapidly applied external stresses or impacts. Therefore although it has relatively good global creep properties at ambient temperature, PMMA is brittle and notch sensitive [Brown, 1991]. Rubber-toughened PMMA (RT-PMMA) has been the focus of commercial and scientific interest for many years [Lovell & Pierre, 1997]. Besides improving the fracture resistance of the polymer, modifiers for PMMA must also maintain the stiffness of the matrix as well as its clarity. Unlike most rubber-toughened polymers, many of the application for rubber-toughened PMMA (RT-PMMA) require optical transparency, with visible light transmission comparable to that of the PMMA matrix. Additionally, for many applications, RT-PMMA competes with polycarbonate,

which has inferior weathering characteristic compared to PMMA. Hence, in designing toughening particles for PMMA it is important to ensure that the weathering properties are not significantly impaired. Good optical properties are achieved by selecting the composition of the polymers forming the rubbery and glassy layers in the particles so that their refractive indices are equal to that of PMMA, thus preventing light scattering by the dispersed particles. Particles on the order of 0.2 to 0.3 μm are normally used. The level of modifier particle present can vary from 10 to 40% by weight of the matrix [Wrottecki *et. al.*, 1991; Mauzac & Schirrer, 1989; Gloagen *et. al.*, 1993; Mauzac & Schirrer, 1990 and Nilesh Shah, 1988]. Nevertheless, as with many other polymers, a significant improvement in the toughness of PMMA can be obtained by combining it with a discrete secondary phase that has a subambient T_g , i.e. a multi-layer particle morphology (core-shell) that consists either of a rubbery core and a glassy shell, or a glassy core, an intermediate rubbery layer, and an outer glassy shell [Paul & Bucknall, 2000]. Since this modifier is rubbery at room temperature it introduces soft, incompressible domains into the matrix. The size of these domains should be chosen to maximize their influence on the intrinsic deformation mechanism of the matrix so as to optimize the rate of energy dissipation during crack development. This approach is currently used to improve the toughness of a wide range of thermoplastics, ranging from amorphous and semicrystalline thermoplastics to highly cross-linked thermosets. In general, RT-PMMA is sold commercially as a final blend, as with HIPS and ABS resins [Lovell & Pierre, 1997].

2.7 Strategies for Toughening

There are two general toughening strategies used for the preparation of rubber-toughening polymers which are preformed spherical particles and interpenetrating polymer networks.

2.7.1 Preformed Spherical Particles

Preformed mono-disperse modifier particles which prepared by emulsion polymerization [Imperial Chemical Industries Ltd., 1967] are widely used to toughen a variety of matrices. Modern rubber-toughened acrylics are manufactured using this technique, spherical particles being added either directly to the acrylic monomer before polymerization or to molten low molecular weight PMMA using a screw extruder. The particle dispersion in the matrix depends on the mixing conditions and on the chemical nature of the particle surface.

For an effective toughening, the efficient of stress transfer between the modifier phases and the matrix is important. The rubbery phase (typically a cross linked copolymer based on either butadiene or n-butyl acrylate) therefore needs to adhere to the matrix [Wrottecki *et. al.*, 1991]. This can be achieved using a core-shell particle structure, illustrated in Figure 2.1, which not only promotes good adhesion to the matrix but also reduces particle agglomeration. The external shell is made from macromolecules that are thermodynamically compatible with the matrix in the melt, grafted on to the rubbery domains of the particles. The strong polymer-polymer interaction resulting from the interpenetration and entanglement of the external shell with matrix ensures adequate adhesion.

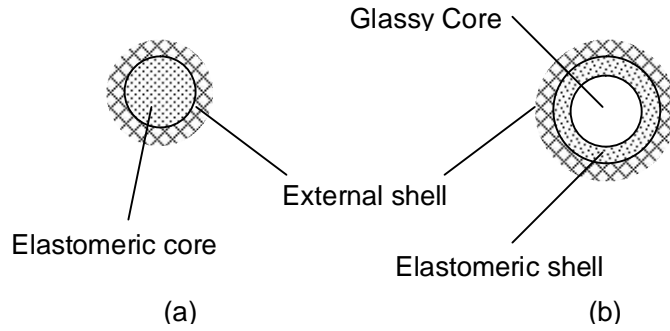


Figure 2.1: Schematic representation of core-shell modifiers; (a) 2 layered core-shell particle and (b) 3 layered core shell particle

The cavitations in the 3 layered particle-modified materials that results from the voiding of the elastomeric shell, is linked to the onset of crazing in the intervening regions of the PMMA matrix [Philippe *et. al.*, 1999]. The initial damage is driven by the negative hydrostatic pressure applied to the particles by the remote stress, consistent with the appearance of small cavities at the poles of the elastomeric shells of the particles. The abrupt increase of stress in the matrix surrounding the particles subsequent to cavitation of the shells may then favor initiation of crazes at the particle equators. The crazes then propagate in the matrix perpendicular to the principal stress axis by the usual mechanism of growth at constant stress in the craze fibrils, as in unmodified PMMA. However, once the crazes penetrate regions whose stress field is strongly influenced by the presence of neighboring particles, they deviate from their initial plane of propagation. In the highly strained regions close to the crack tip, many of the crazes are observed to bifurcate (“craze splitting”), with the trajectories of the craze tips rotating towards the (cavitated) poles of neighboring particles (where the local principal stress axis is also rotated owing to the presence of the free surface). The net result of this is that isolated cavities become linked by the matrix crazes, creating a continuous network of voided material, which will in turn

isolate intervening regions of undeformed matrix from each other [Philippe *et. al.*, 1999]. The accompanying triaxial constraint release may also favor plastic flow in the matrix, leading to high levels of global plastic deformation and blunting at the crack tip prior to crack tip advance, which presumably involves chain scission or chain slip in the craze fibrils (where the true stresses are relatively high).

Craze splitting is efficient in terms of energy dissipation, because it significantly increases the area of fracture as well as contributing to the establishment of a continuous network of craze and cavities. Widespread crazing has been reported elsewhere to occur at crack tips in notched specimens of particle-modified PMMA, where the local triaxiality and strain rates are generally much higher than in simple tension [Mauzac & Schirrer, 1989, Mauzac & Schirrer, 1990]. As summary, there are three main stages of crack tip damage development; 1) cavitation of the rubbery shell or core and craze initiation in the matrix, 2) craze thickening and growth at constant stress and 3) global matrix flow (followed by crack propagation).

2.7.1.1 Core-shell Impact Modifier

Core-shell polymers were commercially introduced as PVC impact modifier in 1958 [Paul & Bucknall, 2000]. Since that time, their use has continuously expanded into new toughening applications, which now include a wide variety of engineering polymers. A major distinction between core-shell particles and other types of impact modifiers is that their size is set during the synthesis process and remains the same after they are dispersed in a host matrix, whereas the final particle

size of linear polymers and bulk rubbers after blending depends largely on processing conditions.

The typical architecture of core-shell polymers have a soft core, made up of rubbery polymer, and is surround by a “shell” of rigid polymer that is grafted to the core. This central nucleus of the particle provides the soft second phase that induces toughening. The shell of the particles occasionally referred to as the outer or hard stage consists of a polymer that is chemically grafted onto the core and generally has a much higher glass transition temperature, T_g than that of the core [Walker & Collyer, 1994]. The shell polymer has 2 primary functions. First, it must allow isolation of the particles from the emulsion by providing a hard coating that keeps the rubbery cores from adhering to one another during the drying process. Second, as the particles are dispersed in the host matrix, the shell functions as the layer that physically binds the matrix to the rubber core.

2.7.2 Interpenetrating Polymer Networks

In previous section, the impact modification of PMMA by the mechanical blending of a low-molecular-weight matrix with preformed particles can only be achieved by a process involving shear deformation, such as extrusion or melt-mixing. However, shear deformation is not involved in the casting process, which is another common means of manufacturing acrylic-based products; the in-situ formation of interpenetrating polymer networks (IPNs) during casting represents an alternative means of producing rubber-toughened materials. The term IPN refers to the permanent interlocking of two or more different polymers, formed by interstitial polymerization [Sperling, 1981]. The synthesis involves mixing all the monomers or

prepolymers, together with their corresponding cross-linking agents, either simultaneously or sequentially. The final morphology of an IPN generally consists of a fine dispersion of distinct phases, as opposed to an interpenetrating network at the molecular level.

In the IPNs, no craze formation is observed [Philippe *et. al.*, 1999]. High magnification TEM observations show that cavitation exists but is initiated in star-shaped regions of the rubbery phase (corresponding to the network nodes). The volume of the matrix elements isolated by the rubbery ligaments is in the same order of magnitude as that observed in the crazed particle-modified PMMA. Thus it is expected that close to the crack tip, the trajectories are rotating towards the poles of neighboring particles. The net result of this is that isolated cavities become linked by the matrix crazes, creating continuous network of voided materials, facilitated by release of the local triaxial constraints. Moreover, to achieve connectivity of the crazes and cavitared particles, and hence to reach an equivalent stress state to that of the cavitared IPN, the matrix of the particle-filled materials must undergo considerable crazing, whose kinetics will in turn be influenced by the temperature and strain response of the matrix.

2.8 Toughening Mechanism

There are different mechanisms for toughening that has been proposed but all rely on a dispersion of rubber particles within the glassy matrix.

2.8.1 Energy absorption by rubber particles

Merz [Merz *et. al.*, 1956] first proposed the idea of rubber particles absorbing energy in order to toughen polymers. They observed that in HIPS an increase in volume and stress whitening accompanied elongation of the material and concluded that these phenomena were associated with the formation of many micro cracks. It was suggested that the fibrils of styrene-butadiene copolymer bridged across the fracture surface of a developing crack and in so doing prevented the crack growing to a catastrophic size. This resulted in more energy being absorbed than an equivalent volume of the polystyrene matrix. The amount of energy absorbed in impact was attributed to the sum of the energy to fracture the glassy matrix and the work to break the rubber particles.

However, the main disadvantage of these proposed theories is that they are concerned primarily with the rubber rather than with the matrix. It has been calculated [Bucknall, 1978] that the total amount of energy associated with the deformation of the rubbery phase accounts for no more than a small fraction of the observed enhanced impact energies. Consequently, this mechanism plays only a minor role in the toughening of multiphase polymers. Further toughening theories concentrated on the deformation mechanism associated with the matrix, which are enhanced by the presence of the rubber phase.

2.8.2 Matrix crazing

Rubber particles have been shown [Bucknall, 1978, Donald & Kramer, 1981] both to initiate and to control craze growth. Under an applied tensile stress, crazes are initiated at points of maximum principal strain, typically near the equator of

rubber particles (maximum concentration of triaxial stresses), and propagate outwards normal to the maximum applied stress, although interactions between the particles' stress fields can introduce deviations. Craze growth is terminated when a further rubber particle is encountered, preventing the growth of very large crazes. The result is a large number of small crazes in contrast to a small number of large crazes formed in the same polymer in the absence of rubber particles. The dense crazing that occurs throughout a comparatively large volume of the multiphase material accounts for the high energy absorption observed in tensile and impact tests and the extensive stress whitening which accompanies deformation and failure. Microscopy studies, both optical and electron, while confirming that crazes frequently initiate from the rubber particles, have aided in elucidating further information concerning the constituents of a craze and the detailed mechanisms of craze initiation, growth and breakdown around rubber particles.

Although a craze appears to be similar to a crack owing to this lower refractive index than its surroundings, it actually contains fibrils of polymer drawn across, normal to the craze surfaces, in an interconnecting void network [Beahan *et. al.*, 1973, Kramer, 1982, Brown, 1979]. The void network is established at the craze tip. The craze tip advances by a finger-like growth produced by the meniscus instability mechanism [Beahan *et. al.*, 1973]. The fibrils are formed at the polymer webs between void fingers and contain highly oriented polymer with the chain axis parallel to the fibril axis [Beahan *et. al.*, 1973; Moore, 1971]. As the craze tip advances the craze thickness by drawing in more polymer from the craze surfaces. It is the presence of the relatively strong craze fibrils that makes the craze load bearing and consequently differing from a crack. Cracks can form, however, by the

breakdown of craze fibrils to form voids. These voids expand slowly by the rupture of surrounding craze fibrils until the void becomes a crack of critical size that can propagate catastrophically.

2.8.3 Shear yielding

Shear yielding in the matrix phase also plays a major role in the mechanism of rubber toughening in polymer blends. Shear yielding, as localized shear bands or more generalized and diffuse regions of shear yielding, usually occurs in addition to elastic deformation. Not only does this phenomenon act as an energy absorbing process but the shear bands also present a barrier to the propagation of crazes and hence crack growth [Bucknall, 1978], therefore delaying failure of the material.

Newman and Strella [Newman & Strella, 1965] first proposed that shear yielding in the matrix was responsible for rubber toughening. Mechanical property and optical property studies, on ABS materials, showed that in tensile tests necking, drawing and orientation hardening occurred together with localized plastic deformation of the matrix around the rubber particles, indicative of shear yielding. It was proposed that the function of the rubber particles was to produce enough triaxial tension in the matrix so as to increase the local free volume and consequently to initiate extensive shear yielding and drawing of the matrix.

However, it is now generally accepted that the shear yielding mechanism constitutes cavitation of the rubber particles followed by extensive shear yielding throughout the matrix [Borggreve *et. al.*, 1989, Yee & Pearson, 1986, Pearson & Yee, 1986, Parker *et. al.*, 1990]. The cavitation of the rubber particles explains the