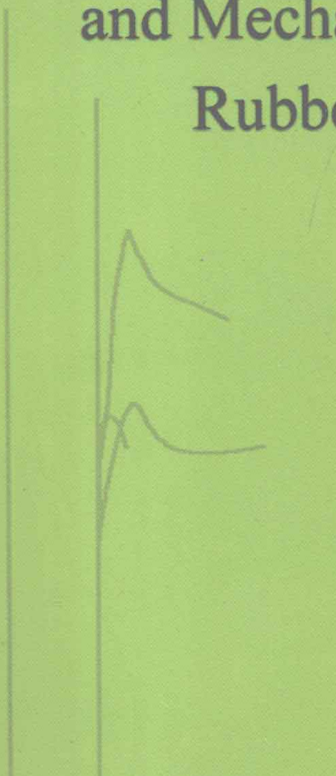
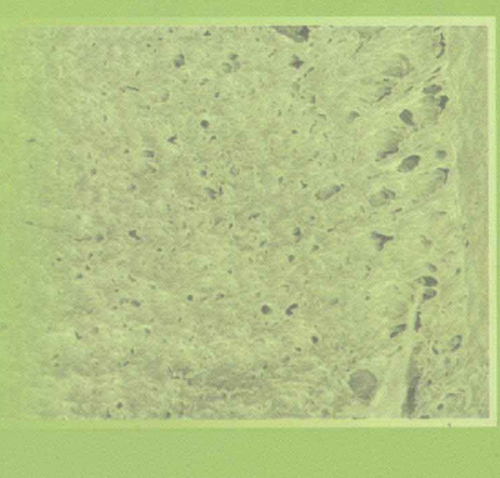
Fracture Surface Morphology and Mechanical Behavior of Rubber-PMMA Composites



Shiyun Gong



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Preface

Why this book written? The primary reason is this. To the best of my knowledge, few books currently available address systematically fracture surface morphology and its correlation with mechanical properties of polymeric materials. Furthermore, few books present methods and procedures both in formulating the mechanical data obtained to reach an equation and in determining the volume fraction of particles in polymer-based composites based on the information obtained from preprocessed TEM images. I have written this book to fill the field.

This book is intended for the professionals and graduate students who work on morphological analysis and characterization of materials.

The book contains 9 parts. Part outlines are as follows. In Part 1, the rationale of the book is explained, and the polymeric materials used and experimental procedure employed for the tensile tests are introduced. Parts 2, 3 and 4 discuss the mechanical properties, stress whitening related analysis, and fracture properties of the rubber-PMMA composites, respectively, with corresponding basic concepts included. Part 5 presents the TEM examination results of rubber-PMMA composites, with SEM and TEM principles introduced. Parts 6 and 7 cover morphological analysis of the fracture surfaces of both unnotched specimens and notched specimens, and the correlations between fracture surface features and mechanical properties. In Part 8, Young's modulus data obtained at low to medium range of crosshead speeds in the rubber-PMMA composites are further analyzed and formulated to reach an equation for Young's modulus as a combined function of strain rate and rubber content; the data analysis and formulation processes by means of rule of mixtures and curve fitting with MATLAB are demonstrated. Part 9 deals with determination of volume fraction of the rubber particles in the rubber-PMMA composite, based on the information obtained from TEM images presented in Part 5. The procedure for preprocessing the TEM images and subsequent statistical analysis are presented in this part.

I would like to express my gratitude to all those who made contribution to this book. The encouragement of my colleagues, especially Sri Bandyopadhyay of University of New South Wales, and support of my family are deeply and sincerely appreciated.

Your comments and suggestions for improvements to this book are important and can be made through corresponding directly with the author.

Shiyun Gong
Harbin University of Science and Technology,
Harbin 150040, China
shiyun@yahoo.com

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Contents

1 Background, Polymeric Materials and Experimental Procedures

1.1 Background

A research project was carried out, to investigate correlations both between mechanical (and fracture) properties and fracture surface features, using unnotched and notched (both blunt notched and sharp notched) composites containing rubber i.e. rubber-toughened polymers, in low to medium range of crosshead speeds.

The primary reason for conducting this project was that some aspects or problems in rubber-toughened materials have not been explored adequately and systematically. Here are some of problem examples. It is known that toughened plastics are viscoelastic in nature, and test speed has a significant effect on test results; however, medium-to-high test speeds have generally been employed in the literature mostly because these tests are less time-consuming (hence less expensive) and this has left a significant gap in data in the lower range of test speeds. Second, it is known that a notch can markedly reduce fracture stress of a brittle glassy polymer like poly(methyl methacrylate) and make ductile materials like rubber-toughened PMMA fail in a brittle manner; however, it is little known how the difference in the fracture surface morphologies for two modes of fracture looks like.

The present author takes the view that study of toughened polymers should be investigated from a broader point of view. This means not only that both conventional unnotched and fracture mechanics-based notched tests need to be carried out experimentally on the same materials under identical test conditions to get comparative and meaningful results, but also that extensive scanning and transmission electron microscopic studies need to be carried out systematically in later stage to obtain correlation between macroscopic properties and microscopic features in fracture surfaces of test specimens to identify and support/complement findings of mechanical test results and get a global understanding of the findings.

This research studied commercial grades of toughened polymers as these are the ones available in the open market for use in actual engineering applications. Moreover, the research employs low-to-medium test speeds to fill a significant gap in data in the lower range of test speeds. Particularly, the research devotes attention to the microscopic examination of deformation/fracture features, in an attempt to reveal correlations between macroscopic properties and microscopic features.

The overall research plan is shown schematically in Fig. 1.1. According to this plan, emphasis is also placed on the data analysis. Formulation of the Young's modulus, and determination of volume fraction of rubber particles in the composites based on information obtained from the microscopic examination are done in ways described in the text. However, more work such as fractal analysis of the surface morphology has yet to be attempted to reach quantitative characterization of surface feature of the composites.

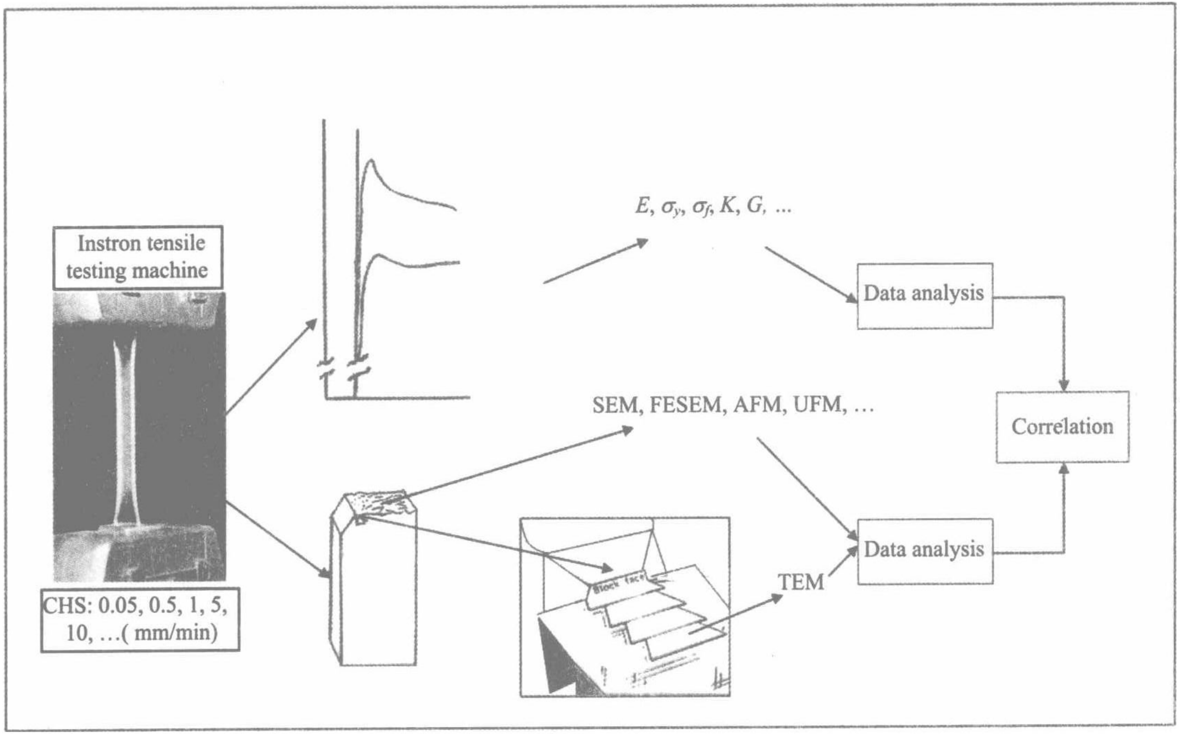


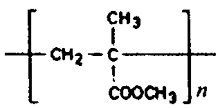
Fig. 1.1 Schematic representation of the overall research plan

1.2 Polymeric Materials

Polymers can be separated into three distinct groups: thermoplastics, rubbers and thermosets. Further, thermoplastics can also be separated into two subgroups: crystalline and non-crystalline (amorphous) among which polystyrene (PS), poly (methyl methacrylate) (PMMA), poly (vinyl chloride) (PVC), polycarbonate (PC) and esters of cellulose are main chemical types of polymer glasses. Glassy polymers are hard and transparent, and many glassy thermoplastics also display another characteristic of glasses—brittleness, like all thermosetting resins. Toughness can be achieved by the addition of a suitable rubber in glassy polymers. The technology of rubber toughening has been extended to almost all of the commercial glassy plastics such as those mentioned.

1.2.1 PMMA and Rubber-toughened PMMA

The repeating unit of PMMA can be shown as



The commercial PMMA is a transparent and amorphous glass with a T_g of 104℃. It is an amorphous glass below 110℃, and shows brittle failure under 85℃. Three types of PMMA are: (1) sheet, based on high molecular weight polymer, (2) lower molecular weight injection molding material and (3) a one-time commercial copolymer.

The major uses of PMMA arise from its high light transmission and good outdoor weathering properties. It is also a useful molding material for applications where good appearance, reasonable toughness and rigidity are required. The material is suitable for display signs, illuminated and non-illuminated, and for both internal and external uses. PMMA is the standard material for automobile rear lamp housings. Typical values of some properties of PMMA are listed in Table 1.1.

Table 1.1 Typical properties of PMMA [6]

E / GPa	G_{IC} / kJm^{-2}	K_{IC} / $MNm^{-1/2}$	T_g / ℃	Refractive index	Poisson's ratio
2.5	0.5	1.1	104	1.49	0.33

A rubbery phase may be added into pure PMMA to make a rubber-PMMA composite which exhibits enhanced impact strength. Therefore, we often call this composite rubber-toughened PMMA (RTPMMA). Two main approaches which have been used to produce rubber-PMMA composite are (1) copolymerization of methyl methacrylate with a second monomer and (2) the blending of PMMA with rubber which is usually poly(butyl acrylate). Substantial improvements in making the composite have been achieved by preparing toughening particles and the matrix PMMA separately. There are several kinds of toughening agents. The acrylic impact modifiers have been used for RTPMMA. The core-shell impact modifiers often have a methyl methacrylate copolymer outer shell.

The toughening particles, prepared by emulsion polymerization, typically comprise two to four radially alternating rubbery and glassy layers. These particles are cross-linked during their formation so that they retain their morphology and size during blending with PMMA and subsequent molding of the blends. This route to RTPMMA allows independent control of the properties of matrix PMMA and the composition, morphology, and size of dispersed rubbery phase.

There are several types of structures for the toughening particles. Fig. 1.2 shows a structure for multiple-phase toughening particles with radially alternating rubbery and glassy layers which can be blended with PMMA. Besides the core-shell structure of the toughening particles, there are still other types of structures. Fig.1.3 illustrates some of the commonest morphologies.

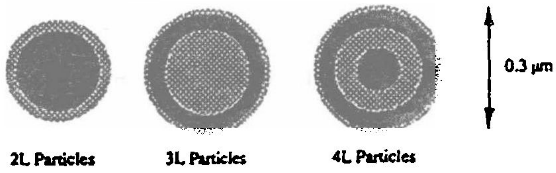


Fig.1.2 Schematic diagrams of sections through the equators of the 2L, 3L and 4L toughening particles[9]
(Rubbery layers are shown in black and glassy layers are cross-hatched)

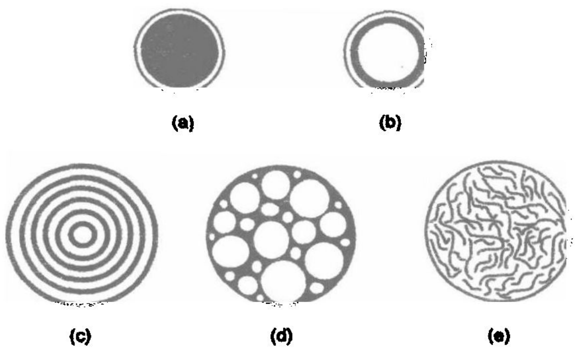


Fig.1.3 Schematic diagram showing typical morphologies of toughening particles[7]
(a) Soft core-hard shell; (b) Hard core-soft shell; (c) Onion morphology; (d) Salami structure; (e) Can of worms morphology

Materials used for making the toughening particles with core-shell structure could be: methyl methacrylate (MMA), ethyl acrylate (EA), *n*-butyl acrylate (BA), styrene (ST), and allyl methacrylate (ALMA) (polymerization grade monomers, Aldrich, ≥98%), potassium persulfate (BDH AnalaR, >99%), and dioctyl sodium sulfosuccinate (Aerosol-OT, Cyanamid). Distilled water was deionized (Eldacan C114) to a conductivity < 0.2 μs/cm before use. The matrix PMMA used for blending with the toughening particles was poly [(methyl methacrylate)-*co*-(*n*-butyl acrylate)] with 8.0 mol % *n*-butyl acrylate repeating units [Diakon LG156(ICI)].

The two-, three- and four-layer (i.e.2L, 3L and 4L) toughening particles, are prepared by sequential emulsion polymerization in which seed particles are first formed and then grown in either two or three stages. The base comonomer formulation used for formation of the rubbery and glassy layers were BA : ST (78.2 : 21.8 mol%) and MMA : EA (94.9 : 5.1 mol%), respectively. ALMA was included in specific constant levels (in the range 0.1 < ALMA < 3.0 mol%) in the comonomer formulations used to form inner layers (i.e., all of the rubbery layers and inner glassy layers).

The effects of particle morphology and rubbery phase volume fraction on fracture properties have been evaluated. The low strain rate values of K_{Ic} for 2L, 3L and 4L RTPMMA materials are significantly higher (2.8 $MPam^{1/2}$) than that of the matrix PMMA (1.22 $MPam^{1/2}$). The properties of rubber-PMMA materials containing 2L toughening particles are generally inferior to those containing 3L or 4L particles.

Acrylonitrile-butadiene-styrene has been used as the toughening media and has resulted in retained transparency of the toughened PMMA. Transparency can be achieved in rubber toughened polymers, either by matching the refractive index of rubber with that of matrix, or by reducing rubber particle diameter below the wavelength of light. A combination of the two techniques is used commercially to make rubber-PMMA material.

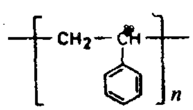
The values of tensile modulus E and Poisson's ratio v for a series of rubber toughened PMMA containing different amounts of rubber are presented in Table 1.2.

Table 1.2 Experimental values of E and v under different rubber contents[10]

Property	V_p / %			
	0	10	20	40
E / GPa	3.4	2.4	2.2	1.5
v	0.34	0.35	0.38	0.40

1.2.2 Polystyrene and High-impact Polystyrene

The repeating unit of polystyrene (PS) can be shown as



Because of its amorphous nature, this commercial polymer has for long been regarded as atactic. The T_gs of the materials are in the range of 90 to 100℃ and isotactic polymers have similar values (approximate100℃). This material is hard and transparent at room temperature. It is widely used as an injection molding and vacuum forming material, and as foam for thermal insulation.