***Morphology and Mechanical Properties of Polycarbonate
/Kraton Blends***

By

Hong Xu

A thesis is submitted to the

Faculty of Graduate Studies and Research

in partial fulfilment of the requirements

for the degree of

Masters of Science

Department of Chemistry

Carleton University

1125 Colonel by Drive

Ottawa, Ontario, Canada

December, 2004

© Copyright, Hong Xu, 2004,

Library and
Archives Canada

Bibliothèque et
Archives Canada

Published Heritage
Branch

Direction du
Patrimoine de l'édition

395 Wellington Street
Ottawa ON K1A 0N4
Canada

395, rue Wellington
Ottawa ON K1A 0N4
Canada

Your file Votre référence

ISBN: 0-494-00792-3

Our file Notre référence

ISBN: 0-494-00792-3

NOTICE:

The author has granted a non-exclusive license allowing Library and Archives Canada to reproduce, publish, archive, preserve, conserve, communicate to the public by telecommunication or on the Internet, loan, distribute and sell theses worldwide, for commercial or non-commercial purposes, in microform, paper, electronic and/or any other formats.

The author retains copyright ownership and moral rights in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author's permission.

AVIS:

L'auteur a accordé une licence non exclusive permettant à la Bibliothèque et Archives Canada de reproduire, publier, archiver, sauvegarder, conserver, transmettre au public par télécommunication ou par l'Internet, prêter, distribuer et vendre des thèses partout dans le monde, à des fins commerciales ou autres, sur support microforme, papier, électronique et/ou autres formats.

L'auteur conserve la propriété du droit d'auteur et des droits moraux qui protègent cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

In compliance with the Canadian Privacy Act some supporting forms may have been removed from this thesis.

Conformément à la loi canadienne sur la protection de la vie privée, quelques formulaires secondaires ont été enlevés de cette thèse.

While these forms may be included in the document page count, their removal does not represent any loss of content from the thesis.

Bien que ces formulaires aient inclus dans la pagination, il n'y aura aucun contenu manquant.

Canada

Abstract

The photoreceptor is an important component in copiers and printers. Since the top layer of the photoreceptor (Charge Transport Layer) is the most prone to mechanical damage, the objective of our study is to enhance the mechanical properties of polycarbonates, which is used in charge transport layer (CTL), by doping with some rubber polymers.

The effect of blending the rubbery copolymer, Kraton, on the morphology and mechanical properties of polycarbonate was investigated. Different types of Kratons (D and G series) were added to the polycarbonate matrix to prepare the films by solution casting with relative weight concentration of Kraton from 2% up to 15%. The morphology changes of Kraton domains based on solvent effect and phase separation were observed by optical microscope. The average sizes and distribution of Kraton domains were calculated. Scanning electron microscope (SEM) was employed to observe the deformation and relaxation of Kraton domains on fracture edges and fracture surfaces after films failure, which provides useful complementary information about morphology change of Kraton domains based on solvent effect as well. The tensile properties were tested by Instron instrument, according to the ASTM-D882-95a standard. The films were stretched until breaking and the force-displacement curves were obtained. The mechanical parameters, such as strain, stress, elongation, Young's modulus and toughness modulus were characterised, which showed that the improvement or deterioration of mechanical properties of polycarbonate/Kraton blends are related to the morphology of Kraton domains in polycarbonate matrix.

Acknowledgements

The first person I would like to thank is my dear supervisor, Dr. Sundararajan, who gives me much significant guidance and tremendous support as he can. I can not image how I could have completed my research work without him. He is so warm-hearted and noble-minded, I learned such a lot from him in these two years, not only how to do the research, but also how to be a true person. I appreciate him in my whole life.

Furthermore I would say thanks to Dr. Ferdous Khan, who always gives me hand whenever I need help. Thanks to all the members of our group, Patrick Yao, Bindu Tuteja, and Mohammad Moniruzzaman. I feel so happy to work with all you great guys. Thanks for your great help and sincere friendship in these two years.

Thanks Lew Ling for instruction of SEM.

Thanks Dr. Marc A. Dube and his student Renata Jovanovic at Ottawa University for help in running Instron instrument for tensile testing.

Thanks NSERC and Xerox Research Center of Canada for financial support and Chemcentral Corporation for providing the Kraton samples for our research purpose.

Thanks a lot to my family. My husband supports my study and work all along. My respectable mother – in – law came from China to help me taking care of my new baby, so that I can save a little time everyday to finish my thesis writing. Thanks my little boy, he let me know how wonderful feeling to be a mother. Thanks all of my friends and relatives. It is all of you to give me strength to work hard, to do my effort to pursue what I want. I love all of you.

Commonly Used Polymer Abbreviations

ABS	Acrylonitrile – butadiene – styrene copolymer
CTBN	Carboxy-terminated butadiene nitrile
HIPS	High impact polystyrene
HPB	Hydrogenated polybutadiene
LDPE	Low density polyethylene
MA	Maleic anhydride
PA	Polyamide
PBT	Poly (butylene terephthalate)
PC	Polycarbonate
PCL	Poly (ϵ - caprolactone)
PECH	Poly (epichlorohydrin)
PP	Polypropylene
PPE	Polyphenylene ether
PPO	Poly (phenylene oxide)
PS	Polystyrene
PVC	Poly (vinyl chloride)
SAN	Styrene – acrylonitrile copolymer
SBS	Styrene-butadiene-styrene triblock copolymer
SEBS	Styrene-ethylene / butylene-styrene
SEP	Styrene-ethylene/propylene
SIS	Styrene-isoprene-styrene

TABLE OF CONTENTS

Abstract	iii
Acknowledgements	iv
List of Abbreviations	v
Table of Contents	vi
List of Tables	x
List of Figures	xi
Chapter 1: Chapter I Introduction to Polymer Blends.....	1
1.1 Polymer blends.....	1
1.2 Compatibility of polymer blends.....	2
1.3 Compatibilizers in polymer blends.....	6
1.3.1 How a compatibilizer functions.....	6
1.3.2 Types of compatibilizers.....	7
1.3.2.1 Non-reactive compatibilizer.....	7
1.3.2.2 Reactive compatibilizer.....	8
1.3.3 Advantages of using the compatiblizer.....	11
1.4 Purpose of the project.....	12
1.5 Thesis overview.....	13
Reference.....	14
Chapter 2: Materials and Methods.....	17
2.1 Materials for Matrix –Bisphenol A Polycarbonate	17
2.2 Materials for blending –Kraton polymers.....	19
2.2.1 Kraton D series.....	20

Table of Contents continued

2.2.2	Kraton G series.....	22
2.3	Unique structure of Kraton polymers.....	24
2.4	The Kraton used.....	24
2.5	Preparation of polycarbonate / Kraton blends.....	25
2.6	Measurement of thickness of films.....	26
2.7	Analytical methods used.....	28
2.7.1	Polarizing Optical Microscopy.....	28
2.7.2	Scanning electron microscope (SEM).....	30
2.7.3	Optical V.S. Electron Microscopy.....	32
2.7.4	Tensile testing for mechanical properties.....	34
2.7.5	Standard apparatus for tensile testing.....	40
	Reference.....	42
Chapter 3: Morphology and domain size analysis of polycarbonate / Kraton blends.....		44
3.1	Morphology of polycarbonate/Kraton blends.....	44
3.2	Analysis of Kraton domain size.....	49
3.3	Change of Shape factor after film failure.....	53
3.4	Analysis of Kraton domains in the annealed films.....	55
3.5	Effect of compatibilizers	59
3.6	Morphology of Kraton D series at fracture edge and surface.....	61
3.7	Morphology of Kraton G series at fracture edge and surface.....	64
3.8	Toughening Mechanism.....	66

Table of Contents continued

Reference	69
 Chapter 4: Mechanical properties of BPAPC/Kraton polymer blends	
4.1 Standard Operation Procedure.....	70
4.1.1 Test Specimens.....	70
4.1.2 Speed of Testing.....	71
4.1.3 Testing Procedure.....	72
4.2 Mechanical Property Results.....	73
4.2.1 Stress – strain curves.....	73
4.2.2 Strength of polymer blends films.....	76
4.2.3 Elongation of the films at break.....	76
4.2.4 Young’s Modulus.....	77
4.2.5 Toughness Modulus.....	81
4.2.6 Abrasion Resistance.....	83
4.3 Strength V.S. Toughness.....	86
4.4 Factors Affecting the Mechanical Properties.....	86
4.4.1 Types of Kraton.....	86
4.4.2 Solvent effect.....	87
4.4.3 Kraton Domain Size.....	88
4.5 Effect of annealing.....	92
Reference.....	94
 Chapter 5: Conclusion and Recommendation for Future Work.....	
5.1 Conclusion.....	95

Table of Contents continued

5.2	Recommendation for Future Work.....	96
5.2.1	Suitable Compatibilizer.....	96
5.2.2	Instron testing with adjustable temperature.....	96
5.2.3	Trials on other Kraton type.....	97
Appendices		98

LIST OF TABLES

Table 2.1	Physical properties for different KRATONS used.....	25
Table 3.1	Solubility parameters of solvents and polymers used.....	46
Table 3.2	Kratons domain size (μm) in the polycarbonate films at various concentrations based on solvent effect (CH_2Cl_2 and CHCl_3).....	50
Table 3.3	The shape factors of Kraton domains in the Polycarbonate / Kraton blends at 98/2 wt % based on solvent effect.....	54
Table 3.4	The Kraton domain size of Polycarbonate /Kraton blends at various anneal temperature in the films made from CH_2Cl_2 and CHCl_3	56
Table 4.1	Speed of Testing.....	72
Table A-1	The strength and standard deviation of BPAPC / Kraton polymer blend films made from CH_2Cl_2 and CHCl_3 at yield points and break points.....	98
Table A-2	The elongation and standard deviation (S.D.) of the BPAPC / Kraton films made from CH_2Cl_2 and CHCl_3	101
Table A-3	The Young's modulus and toughness modulus of the BPAPC / Kraton films made from CH_2Cl_2 and CHCl_3	103
Table A-4	The resilience modulus and abrasion resistance of the BPAPC / Kraton films made from CH_2Cl_2 and CHCl_3	105

LIST OF FIGURES

Figure 1.1	Glass transition temperature of PS/PPO blend.....	3
Figure 1.2	The correlation between T _g and composition for miscible, compatible and immiscible polymer blends.....	5
Figure 1.3	The comparison of SEM picture of PP /PA system.....	8
Figure 1.4	Anhydride end-capped PPO compatibilizer for PPO/PBT reactive blends.....	11
Figure 1.5	Schematic of a typical photoreceptor.....	13
Figure 2.1	Chemical structure of bisphenol A polycarbonate.....	18
Figure 2.2	Schematic of Kraton D series structures.....	21
Figure 2.3	Illustration of three-dimensional SBS network.....	22
Figure 2.4	The schematic for the composition of Kraton G series.....	23
Figure 2.5	The picture of the film coater.....	26
Figure 2.6	SEM micrograph showing the edge of the BPAPC film.....	27
Figure 2.7	SEM micrograph showing the edge of the polycarbonate / Kraton D 1102.....	27
Figure 2.8	Polarized Optical Microscope Configuration.....	28
Figure 2.9	Scheme of Zeiss Axioplan 2 Imaging Universal Microscope.....	29
Figure 2.10	Scheme of SEM with secondary electrons forming image on	

LIST OF FIGURES Continued

	TV screen.....	31
Figure 2.11	The picture of JSM-6400 Digital SEM.....	32
Figure 2.12	Contrast graphs of radiolarian at the same magnification.....	33
Figure 2.13	Depth of focus for a single lens.....	34
Figure 2.14	Schematic of fixture of Instron tester.....	36
Figure 2.15	The picture of Instron tester (Model 1101).....	37
Figure 2.16	Various regions and points on the stress-strain curve.....	38
Figure 2.17	The schematic of the toughness of material.....	39
Figure 3.1	Morphology of Kraton D series domains in the BPAPC (98/2 wt %) films cast from CH ₂ Cl ₂ and CHCl ₃	47
Figure 3.2	Morphology of Kraton G series domains in the BPAPC (98/2 wt %) films cast from CH ₂ Cl ₂ and CHCl ₃	48
Figure 3.3	the difference solubility parameters between the solvents and polymers.....	46
Figure 3.4	the domain size of Kraton D series prepared from CH ₂ Cl ₂ and CHCl ₃	51
Figure 3.5	the domain size of Kraton G series prepared from CHCl ₃	51

LIST OF FIGURES Continued

Figure 3.6	The domain size distribution of Kraton D 1102 2% in the films made from CH ₂ Cl ₂ and CHCl ₃	52
Figure 3.7	The domain size distribution of Kraton D 1116 2% in the films made from CH ₂ Cl ₂ and CHCl ₃	52
Figure 3.8	The domain size distribution of Kraton G series 2% in the films made from CH ₂ Cl ₂ and CHCl ₃	53
Figure 3.9	The morphology of Kraton D series domains (95/5 wt %) in the films cast from CH ₂ Cl ₂ and CHCl ₃ after annealing at 160 °C for 1hour.....	57
Figure 3.10	The morphology of Kraton G series domains (95/5 wt %) in the films cast from CHCl ₃ after annealing at 160 °C for 1hour.....	58
Figure 3.11	Morphology of Kraton D 1116 and Kraton G 1650 with the SMA and PMMA in the BPAPC made from CH ₂ Cl ₂ and CHCl ₃	60
Figure 3.12	SEM micrographs of BPAPC / Kraton D 1102 (90/10 wt %) at fracture surface and edge after films failure.....	62
Figure 3.13	SEM micrographs of BPAPC / Kraton D 1116 (90/10 wt %) at fracture surface and edge after films failure.....	63
Figure 3.14	SEM micrographs of BPAPC / Kraton G series (90/10 wt %) at fracture edge based on solvent effect.....	64

LIST OF FIGURES Continued

Figure 3.15	SEM micrographys of BPAPC / Kraton G series (90/10 wt %) at fracture surface based on solvent effect.....	65
Figure 3.16	Illustration of several toughening mechanisms take part in rubber-toughened polymers.....	66
Figure 3.17	Fracture zone of BPAPC / Kraton D 1102 (95/5wt %), the fracture edge is located at the right.....	67
Figure 3.18	Scanning electron microscopy of CTBN rubber – modified epoxy showing cavitation of a microtome surface.....	68
Figure 3.19	Cavitations of rubber domains mechanism in BPAPC / Kraton blends.....	68
Figure 4.1	Strain – stress curves of BPAPC / Kraton blends in dichloromethane...	74
Figure 4.2	Strain – stress curves of BPAPC / Kraton blends in chloroform.....	75
Figure 4.3	Stress at break versus Kraton composition percentage for BPAPC / Kraton polymer blends.....	79
Figure 4.4	The correlation between the elongation and Kraton content Percentage.....	78
Figure 4.5	Correlation between Young’s modulus and Kraton composite percentage for the BPAPC / Kraton polymer blends.....	80
Figure 4.6	Toughness modulus versus Kraton composition percentage in the	

LIST OF FIGURES Continued

	BPAPC / Kraton films made from CH_2Cl_2 and CHCl_3	82
Figure 4.7	Schematic of single pin – on – disc machine.....	83
Figure 4.8	The correlation between Kraton domain size and abrasion Resistance.....	85
Figure 4.9	Strain –stress curves of BPAPC / Kraton G series based on solvent effect (CH_2Cl_2 and CHCl_3).....	88
Figure 4.10	Correlation between the Kraton domain size and elongation.....	90
Figure 4.11	Correlation between the Kraton domain size and Young's Modulus.....	90
Figure 4.12	The shrinking of film after annealing at T_g temperature.....	93
Figure A – 1	Domain size distribution of Kraton D 1102 10% and 15% in the films made from CH_2Cl_2 and CHCl_3	106

Chapter I Introduction to Polymer Blends

1.1 Polymer Blends

A polymer blend is defined as a combination of two or more polymers resulting from common processing steps e.g. mixing of two polymers in the molten state, casting from common solvent etc. These preparation methods do not usually lead to chemical bonding between the components.¹

Blending polymers is a convenient route to developing new materials, which combine the excellent properties of more than one existing polymer. This strategy is usually cheaper and less time-consuming than the development the new monomers and/or new polymerization routes, as the basis for entirely new polymeric materials. Polymer blending is scaleable for the commercial production with processing machines, such as twin-screw extruders, which are considered standard industrial equipment.²

In the area of engineering thermoplastic materials, blending polymers has led to a significant number of large-volume products such as PPE/HIPS blends (Noryol), PC/ABS blends (Bayblends), PC/ PBT blends (Xenoy) etc. Because of their broad range of properties, the sales volumes of these polymer blends have increased with higher growth rates than the sales of engineering thermoplastic materials (like polyamides, polyesters and polycarbonates) in recent years. The actual consumption of some most important polymer blends already reached the amount of 300,000 tons annually in 1998 (such as PPE / HIPS

and PC / styrene). These high performance polymer blends are geared to heat resistance, good stability against the solvent and excellent resistance to various environments.

1.2 Compatibility of polymer blends

Most pairs of polymers are usually immiscible. Developing a homogeneous blend system to achieve useful properties soon became the promising direction of research. It was discovered that some polymer pairs were completely miscible to give a homogeneous single phase. A number of polymer blends can generally be divided into three types: miscible, compatible, immiscible.³

In miscible blends, the chain segments of the two polymers are miscible on a molecular level. Such blends have only a single glass transition temperature (T_g), which mainly depends on the composition (Fig. 1.2a). A well known example of a blend which is miscible over a very wide temperature range and in all compositions is PS / PPO that combines the heat resistance, the inflammability and the toughness of PPO with the good processability and low cost of PS.^{4,5,6,7, 8} As shown in Fig 1.1, this type of blend exhibits only one glass transition temperature (T_g), which is between the T_g s of both blend components in a close relation to the blend composition.⁹

Fig. 1.1 Glass transition temperature of PS/PPO blend

A system that is either partially miscible or completely immiscible, but offers attractive performances is often designated as a compatible polymer blend. These blends usually have two glass transition temperatures, which may slightly deviate from the T_g of the blend components (Fig. 1.2b). The deviation of the glass transition temperatures from the T_g of the blend component might be different and depend on the partial miscibility of each component in the other. On a microscopic scale these polymer blends have a phase-separated structure (morphology), which could be of different nature, (like sphere, cylinder, or lamellar) depending on the composition of the blends. Usually the major component forms the matrix phase, wherein domains of the minor phase are dispersed. The size of the dispersed domain is related to the interfacial tension and viscosity ratio between the matrix and dispersed phase.¹⁰ Usually the domain size of the dispersed phase is in the range of 1 to 5 μm . An example is the PC / ABS blends, which combine the heat resistance

and toughness of PC with the low temperature impact, processability, stress cracking resistance and low cost of ABS. The commercially available PC/ABS blends have been found to be useful in many molding applications, particularly in the automotive industry.¹¹ It has been reported in literature that PC is partially miscible with the styrene-acrylonitrile (SAN) copolymer, which is part of ABS.^{12, 13} In this case, the interphase is wide and the interfacial adhesion is good.

The largest group are the immiscible blends, having a completely phase separated structure. Therefore, the glass transition temperatures of the components in the blends are exactly the same as for the pure components (Fig. 1.2c). Immiscible polymer blends usually have a coarse morphology with domain size of several microns. The nature of the interface is the main issue for the mechanical performance of these polymer blends. The lack of interfacial strength in the immiscible blends leads to adhesive failure and poor mechanical properties, so that these blends are useless without being compatibilized. Examples of fully immiscible blends are PA / ABS^{14,15}, PP / PA^{16,17} and PA / PPO^{18,19,20}. All of these blends have become commercially successful, but only after being efficiently compatibilized.

Fig. 1.2 The correlation between T_g and composition for miscible, compatible and immiscible polymer blends

1.3. Compatibilizers in polymer blends

1.3.1 How a compatibilizer functions

Compatibilizers are used to allow blending of immiscible polymers, creating a homogenous mixture. Immiscible materials, like oil and water, will form two phases when mixed together. A compatibilizer works like a surfactant, lowering the interfacial tension between two incompatible polymers and allowing the incompatible materials to blend. While the blend is still in two phases, the compatibilizer allows mixing and stability of the two phases to such an extent that the polymers behave as if they were miscible. The compatibilizer typically is a block copolymer. Each block interacts with one of the other polymers in the blend. Reactive compatibilizers form covalent bonds. Non-reactive compatibilizers do not form bonds but are typically miscible with one of the blend components. Compatibilizers play a big role in enabling the design of various types of blends and giving degrees of freedom to meet specific needs, Polymer blends are used to change impact or flex properties, chemical resistance and thermoformability. The properties of the compatibilized blend exceed that of either component alone.²¹

During the melt mixing procedure the compatibilizer reduces the interfacial tension between the immiscible polymers, which results in a significant size reduction of the dispersed domains. Since the surface of the domain is covered by the compatibilizer, the coalescence rate of the dispersed domain is tremendously reduced, which is helpful to keep the morphology of the material stable during the processing steps.^{22, 23, 24} Thus the

compatibilizers are able to generate and to stabilize a finer morphology.

1.3.2 Types of compatibilizers

1.3.2.1. Non-reactive compatibilizers

The emulsification of polymer blends has been proposed as the most efficient route for obtaining fine phase morphology and good mechanical properties. The best way to validate the concept is the addition of pre-made graft and block copolymers and to investigate the beneficial effects that they can have on immiscible polymer blends. The compatibilization of PE and PS blends by copolymers consisting of HPB (miscible with PE) and PS has been extensively studied.²⁵ Another valuable family of diblock copolymer is based on PCL,²⁶ which is miscible with phenoxy, SAN, PVC, nitrocellulose, PECH and chlorinated polyether.^{27, 28}

The use of graft copolymers is another possible route for the control of the phase morphology and the mechanical properties of immiscible polymer blends. Compatibilizers based on PP and PF (PP-g-PF) were suitable for blends or alloys of PP and PA6. Blends of isotactic PP and PA6 were well compatibilized by PP-g-PF. The PP-g-PF compatibilizer consisting of a low molecular weight PP backbone and with a high content of the high molecular weight PF part was observed to be the most efficient combination. A significant reduction in the average domain size was observed. The uncompatibilized blend of PP/PA had a coarse morphology with an average particle size of 5.3 microns (Fig.1.3 a). This large average domain size confirmed the incompatibility of the two components. In the

compatibilized blends, the PA was well dispersed into the PP phase as small spherical particles. Blends prepared with a 2.5 wt % PP-g-PF compatibilizer resulted in fairly uniform PA domains and further increase compatibilizer concentration can decrease the size to 0.3-1.7 microns (Fig. 1.3 b). Similarly, corresponding improvements in the mechanical properties were observed as the average domain size was reduced.²⁹

a. SEM image of incompatible PP/PA system

b. SEM image of compatibilized PP/PA system with PP-g-PF

Fig. 1.3 the comparison of SEM picture of PP /PA system²⁹

1.3.2.2. Reactive compatibilizer

The addition of a reactive polymer, miscible with one blend component and reactive

towards functional groups attached to the second blend component results in the “in-situ” formation of block or grafted copolymers. This technique has certain advantages over the addition “pre-made block or grafted copolymers”. Usually reactive polymers can be generated by free radical copolymerization or by melt grafting of reactive groups on to chemically inert polymer chains. Furthermore, reactive polymers only generate block or grafted copolymers at the site where they are needed, such as the interface of an immiscible polymer blends. Finally, the melt viscosity of a reactive polymer is lower than that of a pre-made block or grafted copolymer, at least if the blocks of the pre-made copolymer and the reactive blocks are of similar molecular weights. Lower molecular weight polymer will diffuse at higher rate towards the interface. This is of utmost importance in view of the short processing times used in reactive blending which may be on the order of a minute.

In order to successfully apply reactive polymers as block or grafted copolymer precursors, the functionalities must have a suitable reactivity in order to react during the short blending time. In addition, the generated covalent bond must be sufficiently stable to survive subsequent processing conditions.

Addition of end-reactive polymer will generate block copolymer. Because of the reactivity of epoxide end groups with carboxylic acid end groups of PBT, a modified PPO has successfully been used as reactive compatibilizer for PPO/ PBT blends³⁰. In this case PPO – b – PBT copolymer is generated at the interface during melt blending.

Addition of polymers carrying pendant reactive groups as precursors will result in graft

copolymer. Numerous examples have been mentioned in both patents and published literatures. Ide and Hasegawa³¹ melt grafted PP with 1.15 wt% of MA in the presence of peroxide. The addition of 3.6 wt% of this PP-MA to a PP/PA 6 80/20 blend resulted in a raise of the yield stress from 23 MPa for the non-compatibilized blend to 38 MPa for the compatibilized blend.

It is common knowledge that Noryl GTX, General Electric's PPO/PA 6.6/ SBS blend, is compatibilized by reactive processing. PPO is end-capped in solution with trimellitic anhydride chloride, as shown in Fig. 1.4.^{32,33} During melt blending with PA 6.6, the anhydride end groups of PPO react with the amine end groups of PA 6.6, generating PPO – b – PA 6.6 copolymer, whose blocks are linked by an imide- bond. This method is applied on a commercial scale. In the commercial PP/PA blend of Akuloy[®], a PP-g- MA is used as a reactive compatibilizer. Dupont's super tough PA, Zytel ST[®], is impact modified with MA grafted EPDM.

Fig. 1.4 Anhydride end-capped PPO compatibilizer for PPO/PBT reactive blends

1.3.3 Advantages of using the compatibilizer

In the bulk state, the compatibilizers provide a strengthening of the interface, which is an important issue for the toughness of multiphase materials.^{34, 35} Assuming that each block poly (A-b-B) compatibilizer penetrates the parent phase (A and B, respectively) deeply enough to be entangled with the constitutive chains, the interfacial adhesion is enhanced. Good interfacial adhesion is essential for efficient stress transfer from one phase to the other and for prevention of crack initiation at the interface to avoid catastrophic failure.

Compatibilization of immiscible polymer blends is by far the most general and efficient strategy to convert the usually poor multiphase blends into high performance alloys. The implementation of this strategy is very straightforward, since it relies on commercially available polymers and existing processing equipment. As a rule, the suitability of

compatibilization techniques to industrial development depends on the complex interplay of several factors, such as cost, final performance, recyclables and possibly biodegradability.

1.4 Purpose of the project

The photoreceptor is an important component of copiers and printers. The mechanical property of the photoreceptor, which is a multilayer device, plays a critical role in the functional performance of the machine. The typical photoreceptor is shown in Fig. 1.5. The top layer of photoreceptor (Charge Transport Layer) is the most prone to mechanical damage. The CTL consists of a polycarbonate as the binder for photoactive molecules. Adding the rubbery polymer Kraton to the CTL has been shown to enhance the performance of the photoreceptor.³⁶ The objective of this work is to relate the morphology of the polycarbonate/Kraton® blends to the mechanical properties. Additionally we try to find a suitable compatibilizer to control the morphology of BPAPC / Kraton polymer blends, so that we might get further improvement of their mechanical properties.

Fig. 1.5 Schematic of a typical photoreceptor

1.5 Thesis Overview

In chapter 1, we introduced some basic knowledge related to our project, such as polymer blend, compatibility of polymer blend and compatibilizer etc. We describe the materials we used in the experiments and the methods we applied for the results analysis in chapter 2. The micrographs we took by optical polarized microscopy reveal the morphology of Kraton domains formed in BPAPC matrix and the data for the Kraton domain sizes analysis are presented in chapter 3. The SEM images are also displayed to show the Kraton domains on the fracture surface and edge of BPAPC films in this chapter. All the mechanical properties results are described and interpreted in chapter 4. Finally the conclusions are made and suggestions for future work are presented in chapter 5.

References

- ¹ Martuscelli E., Palumbo R., Kryszewski, M. *Polymer Blends*, **1979**, ch.1, p. 1-23 Plenum Press, New York
- ² Koning C. Van Duin, M, Pagnoulie, C. Jerome, R. *Prog. Polym. Sci.* **1998**, 23, 707
- ³ Weber M. *Macromol. Symp.* **2001**, 163, 235
- ⁴ Stoelting J., Karasz, F. E., MacKnight, W. J., *Polym. Eng. Sci.*, **1970**, 10, 133
- ⁵ Lefebvre D. Jasse B. Monnerie L. *Polymer*, **1981**, 22, 1616
- ⁶ Prest W. M., Porter, R. S., *J. Polym. Sci., Polym. Phys. Ed.*, **1972**, 10, 1639
- ⁷ Shultz A. R., Gendron B. M., *J. Appl. Polym. Sci.*, **1972**, 16, 461
- ⁸ Shultz A. R., Gendron B. M., *Polym. Preprint, Am. Chem. Soc., Div. Polym. Chem.*, **1973**, 14, 571
- ⁹ Agari Y., Shimada M., Veda A.. *Polymer* **1997**, 38, 2649
- ¹⁰ Wu, S. *Polym., Eng. Sci.* **1987**, 27, 335
- ¹¹ Lombardo B.S, Keskkula H., Paul D.R. *J. Appl. Polym. Sci.* , **1994**, 54, 1697.
- ¹² Keitz J.D, Barlow J.W, Paul D.R. *J. Appl. Polym. Sci.*, **1984**, 29, 3131.
- ¹³ Mendelson R.A. *J. Polym. Sci. Polym. Phys. Ed.*, **1985**, 23, 1975.
- ¹⁴ Majumdar B, Keskkula H, Paul D.R. *Polymer* **1994**, 35, 5453.
- ¹⁵ Majumdar B, Keskkula H, Paul D.R. *Polymer* **1994**, 35, 5468.
- ¹⁶ Park J.S, Kim B.K, Jeong H.M. *Eur. Polym. J.* **1990**, 26, 131.
- ¹⁷ Gonzalez-Montiel A, Keskkula H, Paul D.R. *Polymer* **1995**, 36, 4587.

-
- ¹⁸ Hobbs, S. Y.; Dekkers, M. E.; Watkins, V. H. *J. Mater. Sci.*, **1989**, 24, 1316.
- ¹⁹ Hseih, D. T.; Peiffer, D. G. *Polymer*, **1992**, 33, 1210.
- ²⁰ Kambour, R. P.; Bendler, J. T.; Bopp, R. C. *Macromolecules* **1983**, 16, 753.
- ²¹ *Plastics, additives and compounding* **2004**, 6, 22
- ²² Scott C.E., Macosko C. W., *J. Polym. Sci., Part B* **1992**, 32, 205
- ²³ Scott, C.E., Macosko C. W., *Polymer* **1994**, 35, 5422
- ²⁴ Nakayama A., Inoue T., Hirao A., Guegan P., Khandpur P., Macosko C. W., *Polym. Prepr.* **1993**, 34, 840
- ²⁵ Fayt R., Jerome R., Teyssie Ph. *J. Polym. Sci. Polym. Chem. Ed.*, **1989**, 27, 775
- ²⁶ Heuschen, J., Jerome, R., Teyssie, Ph., *Macromolecules*, **1981**, 14, 242
- ²⁷ Paul, D. R., Newman, S. *Polymer Blends*, **1978**, vol. 1. Ch. 2, Academic Press, New York
- ²⁸ Olabisi, O., Robeson, L. M., Shaw, M. T. *Polymer – Polymer Miscibility*. **1979**, Ch.3
Academic Press, New York
- ²⁹ Larsen K. Borge, Kotlar H. K., Gustafson C. G., *J. of Appl. Poly. Sci.* **2000**, 75, 335
- ³⁰ Yates J. B. *Eur. Patent* 477549, **1992**
- ³¹ Ide F., Hasegawa A., *J. Appl. Polym. Sci.*, **1974**, 18, 963
- ³² Aycock D. F., Ting S. P., *US Patent* 4600741, **1986**
- ³³ Aycock D. F., Ting S. P., *US Patent* 4642358, **1987**
- ³⁴ Brown H. R. *Macromolecules* **1991**, 24, 2752

³⁵ Creton C, Kramer E.J., Hadziioannou, G, *Macromolecules*, **1991**, 24, 1846

³⁶ Sundararajan P.R., Murti D.K. and Bluhm T.L., *US Patent* 5122429, **1992**

Chapter II Materials and Methods

In this chapter we describe the materials that we used in the experiments and introduce the basic principles of the instruments we employed for characterization of the materials. The methods used for the preparation of the films and the measurement of their thickness are also described.

The materials we used for the matrix is bisphenol A polycarbonate (BPAPC). Various types of Kraton rubber copolymers with different composition percentage were blended in the BPAPC. The morphologies of the Kraton domains in BPAPC were studied by optical microscopy. The average domain sizes and shape factors after the films failure were calculated by the specific software. The scanning electron microscope was employed to observe the morphologies of Kratons on the surface and edges of the films after the films failure. The mechanical properties of the BPAPC / Kraton blends were tested by the Instron tester.

2.1 Materials for Matrix - Bisphenol A Polycarbonate

Polycarbonate resins can be divided in two structural classes: aliphatic (which are not widely used as thermoplastics) and aromatics, which are notable engineering thermoplastics. The most common aromatic polycarbonate, poly (bisphenol A carbonate) (BPAPC) is the most important and widely used¹.

The BPAPC polymer is normally amorphous, having good transparency, high ductility and

impact resistance. The combination of all these characteristics leads to properties as optical clarity and high percent elongation, impact strength, toughness and heat resistance

The bisphenol A polycarbonate (BPAPC) we used was purchased from Aldrich Chemical Co. The average M_w is 64,000 (GPC) and the T_g is 150°C and T_m is 267°C. The chemical structure is shown in Figure 2.1.

Fig. 2.1 Chemical structure of Bisphenol A Polycarbonate

The use of BPAPC is spread in many areas. It is suitable for construction, electrical, automotive, aircraft, medical and packaging applications. It is manufactured, for example, as household and consumer articles, sporting goods, photograph and optical equipment and laser-optical data-storage systems.²

Since BPAPC is amorphous, transparent and has unusually high impact strength, it is ideal for laboratory safety shields, bullet-proof window and so on. Polycarbonate is also thermally stable (it can be molded at temperatures as high as 550-600°C) and self-extinguishing. Other uses include gears, bushings, automotive parts, tableware, food containers, medical appliances, and telephone and electronics parts.

Several polyblends of polycarbonate have been developed as engineering plastics, the most important being those with poly (butylene terephthalate) and acrylonitrile–butadiene

-styrene (ABS) copolymers. There is a considerable body of literature on polycarbonate blends with acrylonitrile–butadiene–styrene (ABS) materials.³ These mixtures represent one of the most commercially important series of blend products because of the excellent balance of physical properties and processing characteristics provided for the cost.

Polycarbonate/poly (butylene terephthalate) (PC/PBT) alloy has been widely used in shaped articles because of its easy processability, good size stability, heat resistance, and solvent resistance.⁴ However, the PC/PBT alloy is brittle and this results in low-impact strength at low temperatures and thus limits its applications. Modifiers such as impact modifiers, compatibilizers, and glass fiber were used to improve the physical properties of the PC/PBT alloy.⁵

2.2 Materials for blending – Kraton Polymers

KRATON is the trade name for a series of block copolymers. They are high performance thermoplastic elastomers engineered to enhance the performance capabilities of a wide spectrum of end products and uses. It was first invented by Shell Chemical Company. The versatility of KRATON polymers is due to their distinctive molecular structure, which can be precisely controlled and tailored to perform in specific applications.

There are currently more than 100 grades of KRATON polymers and compounds within the product ranges: KRATON D, KRATON G, KRATON LIQUID and KRATON IR

polymers. In our experiments, we used four types of Kratons, Kraton D 1102, Kraton D 1116, Kraton G 1650, and Kraton G 1652. They belong to two different D and G series.

2.2.1. KRATON D Series

The KRATON D series consists of a triblock copolymer of styrene with an unsaturated rubber mid-block (styrene-butadiene-styrene, SBS, and styrene-isoprene-styrene, SIS). Kraton D polymers are elastic and flexible. The inclusion of butadiene or isoprene influences the properties of the end product. For example, styrene-butadiene-styrene (SBS) is the material suitable for footwear and the modification of bitumen/asphalt. Styrene-isoprene-styrene (SIS) is preferred for production of pressure-sensitive adhesives. The structure of Kraton D series are described in Fig. 2.2.

Polystyrene is a tough hard plastic and polybutadiene is a rubbery material. When these are part of a block copolymer, the SBS has durability and rubber-like properties. In addition, the polystyrene segments preferentially associate with each other. The polystyrene domains are tied together with rubbery polybutadiene chains. This gives the material the ability to recover its shape after being stretched.

On a microscopic scale, the hard polystyrene domains are embedded in the continuous elastic matrix and act as physical crosslink, as illustrated in Fig.2.3. During processing, in the presence of heat and shear forces or a solvent, the polystyrene areas soften. After cooling or solvent evaporation, the polystyrene domains reform and harden, locking the elastic part in place again. This physical cross-linking and reinforcing effect of the

polystyrene domains can give KRATON polymers high tensile strength and elasticity. In our experiments, both the Kraton D 1102 and Kraton D 1116 have the SBS structures.

Kraton D1102 and Kraton D 1116 are generally used as a modifier of bitumen or thermoplastics and in compound formulations. It is also suitable as an ingredient in formulating compounds for footwear applications and may be used as an ingredient in formulating adhesives, sealants and coatings.

SBS structure

SIS structure

Fig. 2.2 Schematic of Kraton D series composition

Fig. 2.3 Illustration of three-dimensional SBS network

2.2.2. KRATON G Series

KRATON G polymers have a saturated mid-block (styrene-ethylene/butylene-styrene, SEBS and styrene-ethylene/propylene, SEP). They are elastic and flexible with the additional benefits of enhanced oxidation and weather resistance, higher service temperatures and increased processing stability. They provide formulation flexibility and ease of processing in commonly used thermoplastic processing technology, and offers such performance benefits as soft touch, improved grip, and UV stability. SEBS, SEPS and SEP grades are used for sealants and high performance adhesives.

Styrene-ethylene / butylene-styrene (SEBS) triblock copolymer is a commercially important thermoplastic elastomer widely used in various applications, such as adhesives, sealants, coatings, footwear, automotive parts, impact modifiers in engineering plastics and

wire insulation, because of its good balance of mechanical properties along with favorable processibility and recyclability.⁶ The structures of SEBS and SEP are depicted in Fig. 2.4. It has been shown that commercial styrene/rubber block copolymers (SRBC), such as poly(styrene-b-butadiene) (SB), poly(styrene-b-butadiene-b-styrene) (SBS), poly(styrene-b-ethylene-co-butylene-b-styrene) (SEBS), and poly(styrene-b-ethylene-co-propylene) (SEP) can act as compatibilizers for iPP/aPS blends⁷. The compatibilizing effectiveness depends on their structural and constitutional parameters like chemical structure of the rubber block, the number of the blocks, the molecular weights of the blocks and weight ratio of the blocks⁸.

Fig. 2.4 The schematic for the composition of Kraton G Series

KRATON G1650 is used in compound formulations and as a modifier of thermoplastics. It may also find use in formulating adhesives, sealants, coatings and modified bitumens. KRATON G1652 is used as a modifier of bitumen and polymers. It is also suitable as an ingredient in formulating compounds for footwear applications.

2.3 The unique structure of KRATON polymers

The versatility of KRATON block copolymers stems from the unique molecular structure of the linear diblock, triblock and radial polymers. Each molecule of KRATON polymers consists of block segments of styrene monomer units and rubber monomer units. Each block segment may consist of 100 monomer units or more. The most common structures are the linear A-B-A block types: styrene-butadiene-styrene (SBS), styrene-isoprene-styrene (SIS), which is KRATON D polymers, and a second generation of the styrene-ethylene / butylenes - styrene type (SEBS) styrene-ethylene/propylene-styrene (SEPS), which are KRATON G polymers. In addition to the A-B-A type polymers, there are specialized polymers of the radial (A-B)_n type: (styrene-butadiene)_n or (styrene-isoprene)_n, and diblock (A-B) type: styrene-butadiene (SB), styrene-ethylene/propylene (SEP) and styrene-ethylene/butylene (SEB).⁹

2.4 The KRATONS used

We selected different four types of Kratons to blend with polycarbonate during our experiments, which were kindly supplied by Chemcentral Corp. (Guelph, Ontario). The composition of different types has been listed in Table 2.1. Kraton G 1652 is a lower molecular weight version of Kraton G 1650 thermoplastic rubber with very similar physical properties except for lower solution and melt viscosity.

Tab. 2.1 Physical properties for different KRATONS used ⁹

Sample Specification	Solution Viscosity (Pa · s) ^a	Styrene / Rubber Ratio (%)	Polymer Type	Tensile strength (psi) _{b , c}	Elongation (%) ^c
Kraton D 1102	1.2	28/72	SBS linear	4600	880
Kraton D 1116	9	23/77	SBS radial	4600	900
Kraton G 1650	8	30/70	SEBS linear	5000	500
Kraton G 1652	1.35	30/70	SEBS linear	4500	500

a. 25%w toluene solution at 25 °C

b. Measured on films cast from a solution in toluene

c. ASTM D - 412

2.5 Preparation of polycarbonate/Kraton blends

Films were prepared by solution casting on a clean smooth glass plate with dichloromethane or chloroform of laboratory grade respectively at the concentration of 2, 5, 10 and 15 (wt %) of different series of Kratons in polycarbonate. Films were coated on glass substrate using an electrically driven film coater and were covered with an aluminum foil so they could be dried at a very low rate of the solvent evaporation for 24h and then transferred to a vacuum oven at room temperature (20 – 25 °C) for another 24h. The film was then peeled off from the glass substrate. The picture of film coater we used for films preparation is shown in Fig. 2.5.

Fig. 2.5 The picture of the film coater

2.6 Measurement of the thickness of films

The thickness of the film was determined by SEM micrographs of the cross section. From the digital SEM image, the thickness can be measured along the cut edge of the film. Usually for one sample, we took two pictures at different parts. From each picture we select four spots to measure, by using “Northern Eclipse ver.6.0” software, and calculate the average thickness. Thickness of the pure polycarbonate film was $17 \pm 0.2 \mu\text{m}$ (Fig. 2.6) and $20 \pm 0.3 \mu\text{m}$ for the BPAPC / Kraton polymer blends (Fig.2.7), regardless of the type of Kraton added to the polycarbonate matrix.

Fig. 2.6 SEM micrograph showing the edge of the BPAPC film

Fig. 2.7 SEM micrograph showing the edge of the polycarbonate / Kraton D 1102

2.7 Analytical Methods Used

2.7.1 Polarizing Optical Microscopy

Fig. 2.8 Polarized Optical Microscope Configuration

The polarized light microscope is designed to observe and photograph specimens that are visible primarily due to their optically anisotropic character. In order to accomplish this task, the microscope must be equipped with both a **polarizer**, positioned in the light path somewhere before the specimen, and an **analyzer** (a second polarizer), and placed in the optical pathway between the objective rear aperture and the eye pieces or camera port. The typical configuration of an optical microscope is shown in fig. 2.8. Although a polarized optical microscope is shown, we used without polarization since our samples are not birefringent.

In the experiment, all the images were taken in the transmission mode. We use Zeiss Axioplan 2 imaging Universal Microscope (Fig. 2.9) to observe the morphology and distribution of Karton domains formed in polycarbonate under the transmitted mode, and then use image analysis software “Northern Eclipse (version 6.0)” to calculate the average Kraton domain sizes and shape factors after failure and the film with mechanical deformation.

Fig. 2.9 Scheme of Zeiss Axioplan 2 Imaging Universal Microscope

2.7.2 Scanning Electron Microscope (SEM)

The Scanning Electron Microscope (SEM) uses electrons rather than light to form an image. There are many advantages to using the SEM instead of a light microscope. The SEM has a large depth of field, which allows a large part of the sample to be in focus at one time. The SEM also produces images of high resolution, which means that closely spaced features can be examined at a high magnification. Preparation of the samples is relatively easy since most SEMs only require the sample to be conductive. Coating with gold make polymer conductive. The combination of higher magnification, larger depth of focus, greater resolution, and ease of sample observation makes the SEM one of the most widely used instruments in various research areas today.

In the SEM, the image is formed and presented by a very fine electron beam, which is focused on the surface of the specimen. The beam is scanned over the specimen in a series of lines and frames called a raster, just like the (much weaker) electron beam in an ordinary television. The raster movement is accomplished by means of small coils of wire carrying the controlling current (the scan coils). A schematic drawing of an electron microscope is shown in Fig. 2.10.¹⁰

Fig. 2.10 Scheme of SEM with secondary electrons forming image on TV screen

We used a JEOL JSM-6400 Digital Scanning Electron Microscope (Fig. 2.11). We observed the Kraton domains distributed on the fracture edges and surfaces of BPAPC. The photographs we took reveal the morphology of Kraton domains after the films failure, which is consistent with the observation by optical microscope.

Fig. 2.11 the picture of JSM-6400 Digital SEM

2.7.3 Optical V.S. Electron Microscopy

The scanning electron microscope (SEM) is the microscope of choice because of its depth of focus and resolving capability. Examination of figure 2.12 shows a striking contrast between an optical and SEM viewgraph of a radiolarian at the same magnification.¹¹ In the optical micrograph taken at high resolution only a section of the radiolarian is in sharp focus. In the lower SEM image the whole specimen is in focus.

a. Optical Microscope viewgraph

b. SEM viewgraph

Fig. 2.12 Contrast graphs of radiolarian at the same magnification

For the optical microscope, the depth of focus is the distance above and below the image plane over which the image appears in focus, which is showed in Figure 2.13. As the magnification increases in the optical microscope the depth of focus decreases. As one goes to higher and higher magnifications, the depth of field in the sample gets smaller and smaller. It becomes hard to keep the entire specimen in focus. Low-power microscopes have greater depth of focus than do high-power microscopes.

The three-dimensional appearance of the specimen image is a direct result of the large depth of field of the SEM. It is this large depth of field in the SEM that is the most attractive feature of the scanning electron microscope. This field arises because of the method in which the data is obtained with a fine electron beam scanned over the surface and with the detected secondary electrons forming an image on the "TV"-like monitor.

This method limited the SEM is applicable to reveal the surface features of the samples, however the optical microscope can provide the morphology information within the bulk sample under the transmission mode. Because of this limitation, the properties such as birefringence can not be determined with the SEM.

Fig. 2.13 Depth of focus for a single lens

2.7.4 Tensile Testing for Mechanical Properties

The tensile test is the most widely used mechanical property test. The intent is to measure inherent material behavior. This exercise is based on the **American Society for Testing and Material (ASTM)** standard tensile test. The axial loads which are applied to the specimen and the corresponding deformation are measured and stresses and strains are calculated during the process. From the stress and strain data, a stress-strain diagram is obtained. It conveys important information about the mechanical properties and the type of behavior of the material.

The tensile **stress** (σ) on a material is defined as the **force per unit area** as the material is stretched. The cross-sectional area may change if the material deforms as it is stretched, so the area used in the calculation is the original cross-sectional area A_0 . The units of stress are the same as those of pressure. We will use Pascal, Pa, as the units for the stress. In the polymer literature, stress often is expressed in terms of psi (pounds per square inch).

$$\sigma = \frac{\text{force}}{A_0}$$

The **strain** is a **measure of the change in length of the sample**. The strain commonly is expressed in one of two

ways: Elongation: $\epsilon = \frac{L}{L_0} - 1$

Extension ratio: $\alpha = \frac{L}{L_0}$

Stress-strain curve is a plot of stress on the y-axis vs. strain on the x-axis. Stress-strain curves are measured with an instrument designed for tensile testing. In a tensile test, a sample of known dimensions (including thickness) is held between two clamps, as shown in figure 2.14.¹² We can refer to the figure 2.15 for the true appearance of Instron tester. As the sample is stretched, the force exerted by the instrument and the length of the sample are

measured. This data can be used to construct a stress-strain curve and to calculate several mechanical properties of the polymer.

Fig. 2.14 Schematic of fixture of Instron tester

As the load is applied, initially the stress-strain diagram is almost a straight line (See fig. 2.16). On unloading, the specimen will return to its previous status. We call the deformation in this area **elastic**. In this elastic region the slope of the line is called the **Young's Modulus**, or **Modulus of Elasticity** of the material. At a certain load plastic deformation starts, that point is called the **yield point**.

Fig. 2.15 The picture of Instron tester (Model 1101)

Past the yield point, increasing load has to be applied to cause continuing deformation and this is **strain hardening**. For instance, the resistance may increase by dislocation interactions in crystalline materials or by molecular orientation in polymers, which cause stress-strain curve bends upward. The stress needed at any plastic state to cause increased plastic deformation is called the **flow stress**. Stress at a particular state is usually referred to as **strength**. For example, the stress at the start of plastic yielding is the **yield strength**. The stress at fracture is called the **fracture strength**. The engineering or nominal stress reaches a maximum value at the maximum applied load and this stress is called the **ultimate tensile stress (UTS)**.

After reaching the UTS, deformation becomes localized in a **necking** region of the specimen. While the material continues to strain harden, the load necessary to cause continuing deformation decreases since the specimen cross section area decreases quickly enough to overcome the strain hardening effect. Deformation continues up to **fracture**. All the mechanical properties are illustrated in the figure 2.16.¹³

Fig. 2.16 various regions and points on the stress-strain curve

σ_u : ultimate stress; σ_f : fracture stress; σ_y : yield stress; σ_{pl} : proportionality limit

The amount of deformation that the material undergoes before fracture is often called **ductility**. The energy needed to cause deformation depends on the force and displacement

or stress and strain. The area under the stress-strain curve up to a given value of strain is the total mechanical energy per unit volume consumed by the material in straining it to that value. **Toughness** is the energy required to cause fracture. The area under the curve is proportional to the integral of the force over the distance the polymer stretches before breaking, which is described in figure 2.17. The ability of a material to absorb energy when deformed elastically and to return it when unloaded is called **resilience**. This is usually measured by the **modulus of resilience**, which is the strain energy per unit volume required to stress the material from zero stress to the yield stress.

Fig. 2.17 the schematic of the toughness of material

The instrument we used for mechanical properties testing is Instron (Model 1101). A rectangular shaped specimen was cut according to the ASTM-D882-95a standard. Grip length is 50 mm, crosshead speed is 25mm/min and full scale load is 50kg. The width of film was 10mm and thickness, 20 μ m, which was measured by SEM. The average value of tensile testing results was calculated based on at least six samples.

2.7.5 Standard Apparatus for Tensile Testing

Grips – a gripping system minimizes both slippage and uneven stress distribution. Grips lined with thin rubber, crocus-cloth, or pressure-sensitive tape as well as file-faced or serrated grips have been successfully used for many materials. The choice of grip surface will depend on the material tested, thickness, etc. Air-actuated grips have been found advantageous, particularly in the case of materials that tend to neck into the grips, since pressure is maintained at all times, so we use pneumatic side action grips during testing process. Since samples frequently fail at the edge of the grips, the serrated grip padded on the square surface with 1.0 mm tape was found to be superior.

Thickness Gage – a micrometer was used to measure the thickness of films. Usually different parts (above six) of one film were measured and the average values were calculated and used. The thickness of BPAPC films was around 17 μ m and 20 μ m for the thickness for the BPAPC/Kraton blends. These results are conformity with the thickness measurement by SEM.

Specimen Cutter – Razor blades are used to cut the specimens to the proper width and producing straight, clean, parallel edges with no visible imperfections. Devices that use razor blades have proved especially suitable for the materials having an elongation-at-break above 10 to 20%. It is imperative that the cutting edges be kept sharp and free from visible scratches or nicks.

Testing Machines – A testing machine with the constant rate of jaw separation was used. The machine is equipped with a device for recording the tensile load and the amount of separation of the grips; both of these measuring systems should be uniform and capable of adjustment from approximately 1.3 to 500 mm/min in increments necessary to produce the strain rates.

Unfortunately the Instron testing machine that we used is a very old model and the computer part connected with data collection and recording had been out of order, so we can not get any data automatically. The only results we can get are those force-displacement curves plotted on a graph paper during the testing process. We then use special software (Golden Software Grapher 5 Demo) to digitize the graphs and convert that information to data.

REFERENCE

- ¹ Sehanobish K., Pham, H.T. Bosnyak C.P., Polycarbonates in: *polymeric materials encyclopedia*, **1996**, vol.8, p. 5697, CRC Press, USA
- ² Malcolm P. Stevens. *Polymer Chemistry An introduction (third edition)*, **1999**, Ch. 12, p. 346, Oxford University Press
- ³ (a) Lombardo, B. S.; Keskkula, H.; Paul, D. R. *J Appl. Polym Sci.* **1994**, 54, 1697
- (b) Cheng, T. W., Keskkula, H., Paul, D. R., *Polymer* **1992**, 33, 1606
- (c) Freitag, D.; Grigo, U.; Muller, P. R.; Nouvertne, W. in *Encyclopedia of Polymer Science and Engineering (2nd edition)*, **1988**, Vol. 11, p. 648
- (d) Paul, D. R.; Barlow, J. W.; Keskkula, H. in *Encyclopedia of Polymer Science and Engineering (2nd edition)*, **1988**, Vol.12, p. 399
- (e) Keskkula, H.; Pettis, A. A. *US Patent*, **1966**, 3239582
- (f) Suarez, H.; Barlow, J. W.; Paul, D. R. *J Appl Polym Sci.*, **1984**, 29, 3253.
- ⁴ (a) Baron, A. L.; Bailey, J. V. *US Patent*, 4034016, **1977**
- (b) Neuray, D.; Nouvertne, W.; Binsack, R.; Rempel, D.; Muller, P. R. *US Patent*, **1984**, 4482672
- (c) Chung, J. Y. J., Neuray, D.; Witman, M. W. *US Patent* 4554314, **1985**
- ⁵ Tseng, William T. W., Lee, J.S., *J. Appl. Polym. Sci.* **2000**, 76, 1280
- ⁶ Holden G and Legge NR, in *Styrenic Thermoplastic Elastomers*, **1996**, ch.2, p. 11, Hanser Publishers, Munich

-
- ⁷ (a) Hlavata D, Hora k Z, Hromadkova J, Lednický F, Pleska A. *J Polym Sci: Part B: Polym Phys* **1999**, 37, 1647
- (b) Hlavata D, Horak Z, Lednický F, Hromadkova J, Pleska A, Yu V. *J Polym. Sci, Part B: Polym. Phys.* **2001**, 39, 931
- (c) Horak Z, Hlavata D, Fortelny I, Lednický F. *Polym. Eng. Sci.* **2002**, 42, 2042
- (d) Bartlett D.W, Paul D.R, Barlow J.W. *Mod. Plast.* **1981**, 58, 60
- ⁸ (a) Apleby T, Cser F, Moad G, Rizzardo E, Stavropoulos C. *Polym. Bull.* **1994**, 32, 479
- (b) Yang LY, Bigio D, Smith T.G. *J. Appl. Polym. Sci.* **1995**, 58,129
- (c) Taha M, Frerejean V. *J Appl Polym Sci*, **1996**, 61, 969
- ⁹ <http://www.kraton.com/kraton/generic/default.asp?ID=41>
- ¹⁰ Reimer L. *Scanning Electron Microscopy Physics of Image Formation and Microanalysis*, **1998**, ch. 1, p. 2, Springer Press, Berlin
- ¹¹ Goldstein J.I., *Scanning Electron Microscopy and X-Ray Microanalysis*, **1980**, ch.1, p. 23, Plenum Press, New York
- ¹² Charles E. Carraher, Jr. *Polymer Chemistry (fifth edition)*, **2000**, ch. 5, p.150, Marcel Dekker Press. New York
- ¹³ David Roylance. *Mechanics of Materials*, **1996**, Ch. 1, p 30. John Wiley & Sons Inc. New York

Chapter III Morphology and Domain Size Analysis of Polycarbonate/Kraton Blends

In this chapter we describe the morphology of Kraton domains in the polycarbonate matrix studied by optical microscopy. The difference in the morphology due to solvent was observed and we presume the solubility parameter predominates. Kraton domain size distribution and shape factors after the films failure were calculated by the imaging analyzer software – Northern Eclipse (version 6.0). All the samples for optical microscope analysis were cut from the middle part of films to make sure they are the most uniform part of the films.

The morphology of Kraton domains on the fracture surface and edge of the films after failure were observed by SEM as well. Samples were cut and fixed for viewing edgewise on a standard SEM puck or stuck on the SEM tape on the metal plate for the fracture surface study. The results were consistent with those of the optical microscope.

3.1 Morphology of polycarbonate/Kraton blends

Kraton D series (Kraton 1102 and Kraton 1116) form the spherical and uniform domains in the polycarbonate (Fig. 3.1) with polymer blend films made from both dichloromethane and chloroform. It seems the solvent did not affect the morphology in this case. There is a sharp contrast between the Kraton D and Kraton G series (Kraton G 1650, Kraton G 1652). In the films made from CH_2Cl_2 , the Kraton G polymer domains present very irregular and

non-uniform morphology, and considerable spreading is seen in Fig. 3.2 a & c. However, with the films cast from CHCl_3 , the Kraton G polymer formed uniform spherical domains as shown in Fig. 3.2 b & d.

We tried to figure out a qualitative reason for this interesting phenomenon, by taking the solubility parameters (δ) of the solvents and polymers from the literature (listed in Tab. 3.1),¹ and calculate the difference between them. Usually if the difference $\Delta\delta$ between the solvent and the polymer is more than $3.5 \text{ MPa}^{1/2}$, the polymer would not dissolve in the solvent.² The differences in δ between the solvents and polymers are plotted in the Fig. 3.3. We can see that the difference in solubility parameters between dichloromethane and the polymers are more than the difference between the chloroform and the polymers. Meanwhile the difference between the solvent and polyethylene are more distinctive, even the $\Delta\delta$ between the dichloromethane and polyethylene is above $3.5 \text{ MPa}^{1/2}$. This predicts that the SEBS, which includes a polyethylene block, would be more difficult to dissolve in CH_2Cl_2 . That may be the reason why the Kraton G copolymer can form relatively uniform spherical domains in CHCl_3 , however, in CH_2Cl_2 they could not disperse well so they aggregate to form the irregular clumps. Since the $\Delta\delta$ between the polybutadiene and both the solvents is at an intermediate level, the Kraton D copolymers (include SBS) can disperse in both solvents well and form the uniform spherical domains.

Actually a polymer solution is a complicated system; we have to consider all aspects, such as interfacial tensions and the polarity of polymers and solvents etc. All of these factors

affect the polymer solubility in a specific solvent. Although some research work has been done in this area,³ a comprehensive study of all aspects needs to be carried out.

Tab. 3.1 Solubility parameters of solvents and polymers used

Solubility Parameter	Solvent		Polymer			
	CH ₂ Cl ₂	CHCl ₃	polycarbonate	polystyrene	Polyethylene / butylene	polybutadiene
δ (MPa ^{1/2})	19.8	19.0	19.5	18.6	16.2	17.2

Fig. 3.3 The differences in solubility parameters between the solvents and polymers

a. K-1102 from CH_2Cl_2 b. K-1102 from CHCl_3
 c. K-1116 from CH_2Cl_2 d. K-1116 from CHCl_3

Fig. 3.1 Optical microscopy picture showing the morphology of Kraton D series domains in the BPAPC (98/2 wt %) films cast from CH_2Cl_2 and CHCl_3

(*the whole length of scale bar is 25 microns, not just for one division, below is same)

a. K-1650 from CH₂Cl₂ b. K-1650 from CHCl₃
c. K-1652 from CH₂Cl₂ d. K-1652 from CHCl₃

Fig. 3.2 Optical microscopy picture showing the morphology of Kraton G series domains in the BPAPC (98/2 wt %) films cast from CH₂Cl₂ and CHCl₃

(*Background changed to enhance contrast)

3.2 Analysis of Kraton domain size

The arithmetic average of the diameters of Kraton domains were calculated by the imaging analysis software, Northern Eclipse (version 6.0). Fig.3.4 and Fig.3.5 show the trend of Kraton domain size versus the Kraton weight percentage content. We found that the Kraton domain size increases with an increase of Kraton weight percentage in the polymer blends except in the case of Kraton G 1652 domains in polycarbonate cast from CHCl_3 . In the case of BPAPC / Kraton G 1652 made from CHCl_3 system, the domain size decreases up to a concentration of 10% and there is an increase thereafter. This is similar to the upper critical temperature found in colloidal systems.⁴ This could be attributed to the limit of solubility of Kraton G 1652 in the solvent CHCl_3 .

The domain size distribution for Kraton D1102 and Kraton D 1116 at 2 wt% in polycarbonate made from both solvents are shown in Fig.3.6 and Fig.3.7 respectively. The domain size distribution of Kraton G series in the films made from CHCl_3 is shown in Fig. 3.8. It is seen that the Kraton D series domain size in the films made from CH_2Cl_2 is generally smaller and the distribution is narrower than those in the films made from CHCl_3 . This may be due to the polarity of solvents. The carbon backbone of the linear polymer we used in the experiment is basically nonpolar, bonded together only by van der Waals-type force. So they prefer to dissolve in the solvent with less polarity. The polarity index of CH_2Cl_2 is 3.4; it is less than that of CHCl_3 , 4.4. So the Kraton D series gets better dispersion in CH_2Cl_2 than CHCl_3 . As we mentioned above, we have to consider

comprehensively, because the final results always depend on the balance of all the factors.

Kraton G 1650 present better domain size distribution than Kraton G 1652 in the films made from CHCl_3 .

All the domain size results of polycarbonate/Kraton blend at various Kraton content weight percentages based on different solvent effect are listed in Table 3.2.

Tab. 3.2 Kratons domain size (μm) in the polycarbonate films at various concentrations based on solvent effect (CH_2Cl_2 and CHCl_3)

Kraton wt%	K-1102		K-1116		K-1650	K-1652
	CH_2Cl_2	CHCl_3	CH_2Cl_2	CHCl_3	CHCl_3	CHCl_3
2%	5.5	7.8	8.6	16.3	8.0	55.1
5%	9.4	8.6	11.2	21.9	11.3	54.0
10%	11.9	11.8	12.0	23.3	15.9	43.5
15%	14.3	14.9	16.1	26.6	17.1	60.9

Fig. 3.4 The domain size of Kraton D series prepared from CH_2Cl_2 and CHCl_3

Fig. 3.5 The domain size of Kraton G series prepared from CHCl_3

Fig. 3.6 The domain size distribution of Kraton D 1102 2% in the films made from CH₂Cl₂ and CHCl₃

Fig. 3.7 The domain size distribution of Kraton D 1116 2% in the films made from CH₂Cl₂ and CHCl₃

Fig. 3.8 The domain size distribution of Kraton G series at 2% in the films made from CH₂Cl₂ and CHCl₃

3.3 Change of shape factor after film failure

The shape factor (SF) is defined as $(4\pi \times \text{area}) / (\text{Perimeter}^2)$. This parameter gives an indication as to the deviation of an object's shape from perfect circle. Circles have the greatest area to perimeter ratio and this formula will approach a value of 1 for a perfect circle. A thin thread-like object would have the lowest shape factor approaching zero.

We used a film stretcher to stretch the film till it fractured. The deformation of Kraton domains was observed under the microscope and the change of shape factor was measured after the films failure. We calculate the initial Shape factor (from original films), final shape factor (after films failure) and shape change rate (SCR) $((\text{initial SF} - \text{final SF}) / \text{initial$

SF) for all the Polycarbonate/Kraton blends (98/2 wt %) to determine the extent of deformation of the shape of all the types of Kratons. The results are listed in Table 3.3.

Tab. 3.3 The shape factors of Kraton domains in the Polycarbonate / Kraton blends at 98/2 wt % based on solvent effect

Specific sample	In CH ₂ Cl ₂			In CHCl ₃		
	Initial SF	Final SF	SCR (%)	Initial SF	Final SF	SCR (%)
PC/K-1102	0.83	0.56	32.4 %	0.83	0.57	31.3 %
PC/K-1116	0.84	0.68	18.8 %	0.83	0.78	5.6 %
PC/K-1650	-	-	-	0.83	0.71	14.5 %
PC/K-1652	-	-	-	0.86	0.85	1.4 %

From the results listed in Table 3.3, we can find that the Kraton D 1102 has much greater shape change rate (SCR) values than other types of Kratons in the films made from both solvents. This indicates the Kraton D 1102 present much better elastic and flexible properties compared with the other types of Kratons. This excellent elasticity of Kraton D 1102 predicts its promising application in the improvement of mechanical properties of polycarbonate / Kraton polymer blends.

3.4 Analysis of Kraton domains in the annealed films

I anneal the Polycarbonate /Kraton blends films (95/5 wt% and 90/10 wt %) at 140°C, 150°C and 160°C for 1hour and check the change of domain size with the various temperatures. We found some big Kraton domains break into small parts to cause the decreasing trend of Kraton domain size with the increasing annealing temperature, such as Kraton D 1102 and Kraton D 1116 in the films made from CH₂Cl₂. However in some cases, like the Kraton G 1650 and Kraton G 1652 in the films made from CHCl₃, their domain size increased after annealing. We consider it as due to some small domains aggregating to form the bigger ones at high temperature. This causes the domain size to increase or has no distinctive change even at the high temperature.

The Kraton domain sizes at different anneal temperatures are listed in Table 3.4. The morphology of Kraton D series domains after annealing at 160 °C for 1hour at 95/5 wt% is shown in Fig. 3.9 and Kraton G series domains morphology under same conditions is shown in Fig. 3.10. From these pictures we find both fragmented and fused Kraton domains coexist in the annealed films. If the fragmentation of Kraton domains became dominant, the Kraton domain sizes become smaller, otherwise the domains sizes increase or hardly change due to the aggregation among the Kraton domains.

Tab. 3.4 Kraton domain size of Polycarbonate /Kraton blends at various annealing temperatures in the films made from CH₂Cl₂ and CHCl₃

A. Kraton D series domain size(μm) under the various annealing temperature

Annealing temperature	K-1102 from CH ₂ Cl ₂		K-1102 from CHCl ₃		K-1116 from CH ₂ Cl ₂		K-1116 from CHCl ₃	
	5%	10%	5%	10%	5%	10%	5%	10%
original	9.4	11.9	8.6	11.8	11.2	12.0	21.9	23.3
140°C	6.9	8.0	6.2	7.8	8.1	8.6	17.7	23.5
150°C	6.5	6.6	5.9	6.8	7.6	8.3	19.4	19.4
160°C	5.1	6.3	5.7	6.3	6.9	8.1	20.0	25.2

B. Kraton G series domain size (μm) under the various annealing temperature

Annealing temperature	K-1650 from CHCl ₃		K-1652 from CHCl ₃	
	5%	10%	5%	10%
original	11.1	15.9	54.0	43.5
140°C	18.0	25.5	54.5	58.2
150°C	15.7	25.3	51.6	44.3
160°C	11.9	23.8	47.7	34.1

a. K-1102 in the films made from CH_2Cl_2 b. K-1102 in the films made from CHCl_3
 c. K-1116 in the films made from CH_2Cl_2 d. K-1116 in the films made from CHCl_3

Fig. 3.9 Optical microscopy picture showing the morphology of Kraton D series domains (95/5 wt %) in the films cast from CH_2Cl_2 and CHCl_3 after annealing at 160°C for 1 hour

a

b

a. K-1650 in the films made from CHCl_3

b. K-1652 in the films made from CHCl_3

Fig. 3.10 Optical microscopy picture showing the morphology of Kraton G series domains (95/5 wt %) in the films cast from CHCl_3 after annealing at 160 °C for 1 hour

3.5 Effect of compatibilizers

Since we want to control the morphology and size of Kraton domains in polycarbonate, we tried to add some compatibilizer to improve the compatibility between the polycarbonate and Kraton copolymers. We selected PMMA (polymethyl methacrylate) and SMA (polystyrene – co – maleic anhydride) for tentative trial and the ratio of polycarbonate / Kraton / compatibilizer was 90/5/5 wt %. The film was still cast from CH_2Cl_2 and CHCl_3 .

We found that both these polymers (PMMA and SMA) increase the Kraton domain size, especially the PMMA. The films cast from CHCl_3 were very sticky to glass plate and quite hard to peel off. If we peeled forcibly, the films curved severely due to the strong surface strain. These films were not fit for mechanical testing because the strong surface strain has already changed the arrangement of polymer chains in the films. Definitely this will affect the mechanical properties of the films. The morphology of Kraton domain with addition of PMMA and SMA are shown in Fig. 3.11.

Since no obvious improvement is achieved, we gave up the effort. But if we could find some suitable compatibilizer to improve the miscibility between the BPAPC and Kraton copolymers, the mechanical properties shall be improved greatly. So further study could focus in this area.

a. K-1116 (5wt %) in the BPAPC made from CH_2Cl_2

b. K-1116 (5wt %) with SMA (5wt %) in the BPAPC (90 wt %) made from CH_2Cl_2

c. K-1650 (10wt %) in the BPAPC made from CHCl_3

d. K-1650 (10 wt %) with PMMA (5wt %) in the BPAPC (85wt %) made from CHCl_3

Fig. 3.11 Optical microscopy picture showing the morphology of Kraton D 1116 and Kraton G 1650 with the SMA and PMMA in the BPAPC made from CH_2Cl_2 and CHCl_3 solvents

3.6 Morphology of Kraton D series at fracture edge and surface

From the SEM pictures (Fig. 3.12 b & c), we can see that the morphologies of Kraon D series show the spherical domains in either CH_2Cl_2 or CHCl_3 , which has already been proved by the images of optical microscope. Once stretching the films, the Kraton domains deformed from spherical to elliptical. We can observe the elliptical shape of Kraton D 1102 domains on the fracture edge (as shown in Fig. 3.12 a & d). Because Kraton D 1102 toughens the BPAPC and make it more ductile than the other polymer blends, the Kraton D 1102 domains endure the greater deformation than the others during the films stretching; that is why the shape of Kraton D 1102 domains on the fracture edge are elliptical. The morphology of Kraton D 1116 domains on the fracture surface and edge are shown in figure 3.13. It is seems that fibrillation of the domains occurs in this case.

a

b

c

d

a, b films made from CH_2Cl_2 ; c, d films made from CHCl_3

a, d micrographs of fracture edge; b, c micrographs of fracture surface

Fig. 3.12 SEM micrographs of BPAPC / Kraton D 1102 (90/10 wt %) at fracture surface and edge after films failure

a, b films made from CH_2Cl_2 ; c, d films made from CHCl_3

a, d micrographs of fracture edge; b, c micrographs of fracture surface

Fig. 3.13 SEM micrographs of BPAPC / Kraton D 1116 (90/10 wt %) at fracture surface and edge after films failure

3.7 Morphology of Kraton G series at fracture edge and surface

Kraton G series showed different morphologies based on solvent effect. In the films made from CH_2Cl_2 , they present irregular morphology (as shown in Fig. 3.14 a & c), however, they display spherical shape on the fracture edge of the films made from CHCl_3 . The same phenomenon can be observed on the fracture surface as well (as shown in Fig. 3.15).

a, b BPAPC / Kraton G 1650; c, d BPAPC /Kraton G 1652
a, c films caste from CH_2Cl_2 ; b, d films cast from CHCl_3

Fig. 3.14 SEM micrographs of BPAPC / Kraton G series (90/10 wt %) at fracture edge based on solvent effect

a, b BPAPC / Kraton G 1650; c, d BPAPC /Kraton G 1652
a, c films caste from CH_2Cl_2 ; b, d films cast from CHCl_3

**Fig. 3.15 SEM micrographys of BPAPC / Kraton G series (90/10 wt %) at fracture
surface based on solvent effect**

3.8 Toughening Mechanism

Several mechanisms that are responsible for toughening are illustrated in Fig. 3.16⁵. The most commonly observed mechanisms include localized shear yielding, which refers to shear banding in the matrix occurring between the rubber domains, cavitation in the rubber matrix, and rubber domain bridging behind the crack tip.

Fig. 3.16 Illustration of several toughening mechanisms take part in rubber-toughened polymers

From the SEM micrographs, we think there are two deformation mechanisms in our samples. In the case of ductile fracture, voiding of rubber domains and strong shear yielding of the matrix take place. In this yielding process these voids become elongated.⁶ We found the similar phenomenon on the fracture surface of BPAPC / Kraton D 1102 (as shown in fig. 3.17. We can clearly see the shear yielding in BPAPC and voids around rubber domains coexist in the fracture zone. As the fracture edge is approached the voids are more deformed and elongated.

- a. shear yielding in BPAPC matrix between the Kraton domains**
- b. elongated voids around Kraton domains**

Fig. 3.17 SEM micrograph showing the fracture zone of BPAPC / Kraton D 1102 (95/5wt %), the fracture edge is located at the right

Brittle fracture merely gives rise to voids, which are caused by cavitation of rubber domains. The most important mechanism in rubber toughening plastic is now thought to be cavitation and it is studied via scanning electron microscopy as illustrated in see Fig. 3.18. Yee et al⁷ noted that rubber cavitation precedes plastic yielding. At room temperature and at moderate strain rates, the carboxy-terminated butadiene nitrile (CTBN) appears to cavitate well before shear yielding in the matrix. In our experiment, cavitated rubber domains toughening mechanism predominates in the samples other than Kraton D 1102 (as shown in Fig. 3.19). On the fracture zone of BPAPC / Kraton D 1116, we can see several cavities are formed within the large Kraton domain. Usually if the large rubber domains

span the two crack surfaces, the cavitation mechanism only absorbs small energy before the fracture, so the big domain propagates the cracks fast and easily.

Fig. 3.18 Scanning electron microscopy of CTBN rubber – modified epoxies, showing cavitation of a microtome surface

- a. cavitated Kraton domains in BPAPC / Kraton D 1116 (95/5wt%)**
- b. cavitated Kraton domains in BPAPC / Kraton G 1650 (95/5 wt%)**

Fig. 3.19 Cavitations of rubber domains mechanism in BPAPC / Kraton blends

References

- ¹ Sperling, L. H., *Introduction to Physical Polymer Science (second edition)*, **1992**, Ch. 3, p 67, John Wiley & Sons, Inc. New York
- ² Liu F. Q., Tang, X, Y, *Polymer Physics (first edition)*, SS No. 10073499, **1995**, Ch. 3, p 105, Technology Press, Beijing
- ³ (a) Wen-ping Hsu, *J. Applied Poly. Sci.*, **2001**, 80, 2842
- (b) Du Y., Xue Y., Frisch, H. L., in *Physical Properteis of Polymer Handbook*, Mark J. E. Ed. **1996**, ch. 16, Amer. Inst. Phys. Press
- (c) Hansen C. M. in *Macromolecular Solutions: Solvent – Polarity Relationships in Polymer*, **1982**, p.1, ACS Symp. Proc.
- ⁴ Cowie, J. M. G. *Polymers: Physics and Chemistry of Modern Materials*, **1973**, p. 140, Intertext Books, UK
- ⁵ H. R. Azimi, R. A. Pearson, R. w. Hertzberg, *J. Mater. Sci. Lett.*, **1994**, 13, 1460
- ⁶ van der Wal A., Gaymans R. J. *Polymer*, **1999**, 40, 6067
- ⁷ Yee A. F., Li D., Li, X., *J. Mater. Sci.*, **1993**, 28, 6392

Chapter IV Mechanical Properties of BPAPC/Kraton

Polymer Blends

The mechanical properties of all the BPAPC / Kraton polymer blends were studied by tensile testing on the Instron tester (Model 1101) in conformity to ASTM D 882 – 95a. The mechanical properties, such as Young's Modulus, strength, strain, toughness modulus, elongation, were measured by tensile testing. Based on the results, we discuss the correlation between the morphology of Kraton domains and mechanical properties. The fracture mechanism during the stretching process was discussed in this chapter as well.

4.1 Standard Operation Procedure

4.1.1 Test Specimens

A. the test specimen shall consist of strips of uniform width and thickness at least 50mm longer than the grip separation used. The length of the sample we used is more than 100mm.

B. The nominal width of the specimens shall be not less than 5.0 mm or greater than 25.4mm. The width of our specimens is 15mm.

C. A width / thickness ratio of at least eight shall be used. The ratio in our sample is 750 (width/thickness is 15 mm /0.02 mm). Narrow specimens magnify effects of edge strains or flaws.

D. Utmost care shall be exercised in cutting specimens to prevent nicks and tears which are likely to cause premature failure.

E. For tensile modulus of elasticity determinations, a specimen gage length of 250mm shall be considered as standard. This length is used in order to minimize the effects of grip slippage on test results. But this length is not feasible for our sample, the test sections as short as 50mm were used. The speed of testing for shorter specimens is adjusted in order for the strain rate to be equivalent to that of the standard specimen.

G. Conduct tests in the standard laboratory atmosphere of 23 ± 2 °C and $50 \pm 5\%$ relative humidity.

F. In the case of isotropic materials, at least five specimens shall be tested from each sample. Specimens that fail at some obvious flaw or that fail outside the gage length shall be discarded and retests made.

4.1.2 Speed of Testing

The speed of testing is the rate of separation of the two grips of the testing machine when running idle. The speed of testing shall be calculated from the required initial strain rate as specified in table 4.1. The rate of grip separation may be determined for the purpose of these test methods from the initial strain rate as follows:

$$A = BC$$

Where: A = rate of grip separation, mm/min

B = initial distance between grips, mm

C = initial strain rate, mm/mm·min

Tab. 4.1 Speed of Testing

Percent Elongation at Break	Initial Strain Rate mm/ mm·min
Less than 20	0.1
20 to 100	0.5
Greater than 100	10.0

Since most elongations at break of our specimens fall in 20 to 100% range, the initial strain rate (C) shall be 0.5 mm/ mm·min. We assumed the initial distance between grips (B) was 50mm, so the rate of gripe separation (A) was 25mm/min.

4.1.3 Testing Procedure

Select a load range such that specimen failure occurs within its upper two thirds. A few trial runs indicate the proper load range was 0~50 N. We use 50mm for initial grip separation. Since the test strips shall be at least 50mm longer than the grip separation used, the total length of the specimen was more than 100mm. We set the rate of grip separation to give the desired strain rate (25mm/min) between the grips. Take care to

align the long axis of the specimen, tighten the grips evenly and firmly to the degree necessary to minimize slipping of the specimen during test. We found the serrated grips padded on the square surface with 1.0 mm tape can prevent slippage of films from the grips. So we stick the tapes on the surface of the grips for better testing procedure. Run the Instron tester and record load versus grip separation.

4.2 Mechanical Property Results

4.2.1 Stress – strain curves

The average value of tensile testing results was calculated by using at least 6 samples. The strain – stress curves of different types of BPAPC / Kraton polymer blends made from dichloromethane and chloroform are shown in Fig.4.1 and Fig. 4.2. The results we obtained indicate that the addition of Kraton D 1102 to polycarbonate could improve the ductility and toughness of materials greatly, which represented much better mechanical properties contrast with the pure polycarbonate and the other polycarbonate / Kraton polymer blends. This BPAPC / Kraton D 1102 polymer blends demonstrated the much more uniform and delicate morphology (shown in Fig. 3.1) and quite smaller domain size (as shown in Fig. 3.4) compared with the other polymer blends. The delicate morphology with small domain size may absorb more energy on loading, delaying or preventing fracture. The compatible polymer blend BPAPC / Kraton D 1102 predicts a promising application on the improvement of mechanical properties of polycarbonate.

A. BPAPC / Kraton D series (98 / 2 wt %) in CH_2Cl_2

B. BPAPC / Kraton G series (95/5 wt %) in CH_2Cl_2

Fig. 4.1 Strain – stress curves of BPAPC / Kraton blends in dichloromethane

A. BPAPC / Kraton D series (98 / 2 wt %) in CHCl_3

B. BPAPC / Kraton G series (98/2 wt %) in CHCl_3

Fig. 4.2 Strain – stress curves of BPAPC / Kraton blends Prepared from chloroform Solution

4.2.2 Strength of polymer blends films

The strength of the polymer blend films and the values of standard deviation (S.D) are listed in table A-1 (in appendix). All the strength results are average values based on several testing for an individual sample. The standard deviation is a measure of how widely values are dispersed from the average value (the mean). It is calculate by this formula: $\sqrt{\frac{n\sum x^2 - (\sum x)^2}{n(n-1)}}$ (x is specific testing result for individual sample, n is the amount of testing results).

The correlation between the composite percentage of Kraton and stress at break are shown in Fig. 4.3. The overall trend is stress at break decreased with the increasing of the Kraton composite percentage. It is reasonable result since the Kraton domain size increases with the amount of Kraton added to the polycarbonate. The fracture toughness appears to increase with decreasing domain sizes.

4.2.3 Elongation of the films at break

The values of elongation of films and standard deviations are listed in table A-2 (in appendix). The results indicate that the addition of Kraton D 1102 in the BPAPC can improve the ductility of films greatly, especially in the films with Kraton D 1102 at 2 wt%, the elongation can reach to over 100%. Furthermore the films with Kraton G 1650 made from CHCl_3 demonstrated better ductility than the films made from CH_2Cl_2 . This is

because of the change of morphology of Kraton domains in polycarbonate based on solvent effect. However the films with Kraton D 1116 and Kraton G 1652 made from CHCl_3 have less ductility compared with the films made from CH_2Cl_2 ; this is controlled by the Kraton domain size formed in the polycarbonate films. The correlation between the elongation and Kraton content percentage is shown in Fig. 4.4. We can see the addition of Kraton D 1102 in CH_2Cl_2 improved the elongation of the polycarbonate films. Basically the trend for elongation decreased with the increasing Kraton content percentage. But after 5%, the decreasing speed became slow, like Kraton D 1116 in CH_2Cl_2 and Kraton G 1650 in CHCl_3 . Kraton G 1652 still show its special trend, the elongation increased up to 10% and decreased thereafter, which is in conformity with its trend of domain size (see section 3.2).

4.2.4 Young's Modulus

Since the Kraton is a rubbery copolymer, the addition of Kraton will decrease the Young's Modulus of polycarbonate, which means the BPAPC / Kraton polymer blends are not as strong as the pure polycarbonate, but they present more ductility than the pure polycarbonate. So the Young's Modulus of BPAPC / Kraton polymer blends decreased with the increasing of Kraton composition percentage, which is shown in Fig. 4.5. The value of the Young's modulus for a specific BPAPC / Kraton blends does not depend on the solvent used. But the Young's modulus of the films with Kraton D 1116 from CH_2Cl_2 is smaller than that from CHCl_3 , and the former demonstrated better elasticity and greater

elongation than the latter. Obviously this is also because of the various Kraton domains size formed in polycarbonate matrix. The values of Young's modulus for all the samples are listed in the table A-3 (in appendix).

Fig. 4.4 The correlation between the elongation and Kraton content percentage (the standard deviations are listed in appendix)

Fig. 4.3 Stress at break versus Kraton composition percentage for BPAPC / Kraton polymer blends (the standard deviations are listed in appendix)

Fig. 4.5 Correlation between Young's modulus and Kraton composite percentage for the BPAPC / Kraton polymer blends

4.2.5 Toughness Modulus

Toughness is the ability to absorb energy up to fracture. The energy per unit volume is the total area under the strain-stress curve. The general trend is that the toughness modulus of the BPAPC / Kraton films decreased with increasing Kraton composition (as shown in Fig. 4.6). The toughness modulus of Kraton G 1652 in the films with polycarbonate shows an initial increase up to a certain concentration and decreases thereafter. This is similar to the trend shown in Fig. 3.5 for the domains size. All the results regarding the toughness modulus are listed in table A-3 (in appendix) as well. We can find that the films with Kraton D 1102 at 2 wt% have the maximum toughness modulus, which indicated the Kraton D 1102 (at 2wt %) has the best rubber-toughened effect for BPAPC / Kraton polymer blend. This result is conformity with the results we obtained from strengths and elongations of the blends films.

Fig. 4.6 Toughness modulus versus Kraton composition percentage in the BPAPC / Kraton films made from CH_2Cl_2 and CHCl_3

4.2.6 Abrasion Resistance

Abrasion resistance is defined as the ability of a material to withstand mechanical action such as rubbing, scraping, or erosion that tends progressively to remove material from its surface. Such ability helps to maintain the material's original appearance and structure. Abrasive wear studies usually are carried out on a single pin-on-disc machine,¹ the schematic is shown in Fig. 4.7.

Fig. 4.7 Schematic of single pin – on – disc machine

We sent our samples to an external research facility for the abrasive wear testing. Unfortunately our polymer sample's thickness is too thin ($\sim 20\mu\text{m}$) and the films can not attach on the substrate tightly. Once the testing machine started, the films were scratched severely and peeled off from the substrate. Although we were not able to test the abrasive

resistance of the samples, we still tried to figure out the general trend of the abrasion resistance and Kraton domain size for our samples.

There have been qualitative studies relating the Young's modulus and scratch resistance. Hayafune et al.² found that abrasion resistance can be evaluated by the equation $R = 0.25 U (Y/E)$, where R is the predicted abrasion resistance, U is breaking energy (toughness modulus), Y is resilience modulus and E is Young's modulus. The results of abrasion resistance calculated using this equation are listed in the table A-4 (in appendix). The trend between the Kraton domain size and the predicted abrasion resistance are shown in Fig. 4.8. We can see generally R decreased with the increasing Kraton domain sizes; however it is also depend on the types of Kratons. Kraton D series have better abrasion resistance than Kraton G series; especially Kraton D 1102 has the maximum abrasion resistance at 2 wt%. The trend for Kraton G series seems interesting. It first increases with the increasing Kraton domain size, when it reaches to a peak value, and it falls down rapidly. Basically we find the trend of abrasion resistance is conformity with that of toughness modulus. So we consider the tougher material can perform better abrasion resistance as well.

A. Kraton D series in both solvents (CH₂Cl₂ and CHCl₃)

B. Kraton G series in both solvents (CH₂Cl₂ and CHCl₃)

Fig. 4.8 The correlation between Kraton domain size and abrasion resistance

4.3 Strong V.S. Tough

There is a difference between toughness and strength. A material that is strong but not tough is said to be brittle, this material usually has high Young's modulus along with low toughness modulus. Based on the results we obtained, we can find usually the addition of Kratons rubbery copolymers deteriorates the mechanical properties of BPAPC, make the BPAPC / Kraton polymer blends neither strong nor tough, except of the Kraton D 1102. At low composition percentage, 2wt%, the Kraton D 1102 can improve the ductility and toughness modulus of BPAPC greatly and make it strong and tough; this is a typical rubber-toughened plastic effect.

4.4 Factors Affect the Mechanical Properties

4.4.1 Types of Kraton

Compared with Kraton G series we find the Kraton D series presented more efficiency on improvement of the mechanical properties of the BPAPC / Kraton blend films. Especially the BPAPC / Kraton D 1102 (at 2 wt %) polymer blend showed very good mechanical properties. This mainly depends on the differences in the composition and structure among Kraton types. Kraton D 1102 and 1116 have an unsaturated rubber mid-block, SBS, styrene-butadiene-styrene; they show much more elongation values than Kraton G 1650 and 1652 (as shown in table 2.1). Kraton G polymers have saturated mid-blocks, SEBS, and it cause less elasticity structurally.

4.4.2 Solvent Effect

Kraton D series formed regular spherical domains in the BPAPC made from both solvents CH_2Cl_2 and CHCl_3 . However Kraton G series domains have no specific shape and dispersed disorderly in the polycarbonate made from CH_2Cl_2 ; but they displayed relatively regular spherical domains in the films made from CHCl_3 . Especially Kraton G 1650 form more uniform and delicate domains in CHCl_3 than in CH_2Cl_2 , and this results in the mechanical properties of BPAPC / Kraton G 1650 made from CHCl_3 to be much better than those made from CH_2Cl_2 (as shown in Fig. 4.9). We consider that this behavior is because of the difference of solubility parameter (see section 3.1). It indicates the Kraton G 1650 can disperse better in CHCl_3 .

BPAPC / Kraton G 1652 is exceptional. Although the Kraton domains form spherical morphology in BPAPC made from CHCl_3 , the elongation and toughness modulus became worse than those made from CH_2Cl_2 . That is because the oversized Kraton domains form in the BPAPC made from CHCl_3 . Fast crack propagation around the oversized Kraton domains is prone to cause the films failure at even quite low loading. This implies that both the morphology of Kraton domains and Kraton domain size predominate the mechanical properties of BPAPC / Kraton polymer blends.

There exist other factors, such as the interfacial tensions, polarity of polymers and solvents, work together in the complicated polymer solutions. We did not study these factors in this thesis, but obviously more research is required focusing on these aspects.

Fig. 4.9 Strain –stress curves of BPAPC / Kraton G series based on solvent effect (CH₂Cl₂ and CHCl₃)

4.4.3 Kraton Domain Size

For the Kraton D series, since the morphologies of Kraton domains formed in the BPAPC films are spherical in both solvents, the Kraton domain size and size distribution play critical roles in controlling the mechanical properties.

The Kraton D 1102 domains sizes are quite similar from both solvents, but the elongation

and toughness modulus still show distinctive difference. We considered that this could be due to the Kraton size distribution. Usually if the Kraton size distribution falls in a wide range and some large Kraton domains formed in the matrix, it will deteriorate the ductility of the materials. The size distribution of Kraton D 1102 in the films made from CHCl_3 is wider than that in the films made from CH_2Cl_2 , the elongation and toughness modulus of the former are smaller than the latter. One explanation is that large domains tend to span the two crack surfaces, whereas small domains cavitate in a process zone in the vicinity of the crack tips. Spanning the two crack surfaces only provides a small energy absorption mechanism, while cavitation relieves stresses triaxially.³ The figures of the domain size distribution for Kraton D 1102 10 wt% and 15 wt% are shown in the appendix (Fig. A -1), the Kraton D 1102 2wt% was shown in Fig. 3.6.

Kraton D 1116 domain sizes are smaller in the films made from CH_2Cl_2 than those in the films made from CHCl_3 , so the former are tougher and ductile than the later. Generally the elongations and Young's modulus of the films decrease with the increasing of Kraton domain sizes (as shown in Fig. 4.10 and Fig. 4.11).

Fig. 4.10 Correlation between the Kraton domain size and elongation

Fig. 4.11 Correlation between the Kraton domain size and Young's Modulus

(Domain size was varied by changing the concentration of Kraton in polycarbonate)

A number of papers have been reported on the deformation mechanism and fracture behavior of polypropylene-rubber blends to understand the effect of rubber particle size on the fracture behavior.^{4,5,6} Jang illustrated the rubber particle size dependence of crazing in polypropylene.⁷ He found PP blends with smaller rubber particles are tougher and more ductile than those with larger particles, probably because the former represents a more efficient use of rubbery phase in promoting crazing yielding. Samples with average particle diameter $D \geq 0.5 \mu\text{m}$ were found to exhibit pronounced crazing. Within a given sample, no crazes appeared to develop around individual rubber particles with $D < 0.5 \mu\text{m}$. The higher the diameter value, the greater is the propensity to form craze. The behavior of samples with $D \ll 0.5 \mu\text{m}$ appeared to be dominated by shear yielding; very few crazes could be found. Small particles, inducing smaller stress-enhanced zones, are therefore not effective in initiating crazes.

We observed similar results although the average Kraton domain diameters in our samples are much bigger than Jang's. In our experiment generally the films with Kraton domain diameter $D < 10 \mu\text{m}$ became tougher and more ductile than the pure polycarbonate films; when the diameter of Kraton domains $D > 10 \mu\text{m}$, the films tend to failure easily. From the SEM micrographs (Fig. 3.12) we observed the Kraton D 1102 domains deformed much, the morphology of Kraton domains on the fracture edge changed the shape from spherical to oval. Since they have smaller domain size which induce smaller stress enhanced zone, they can absorb much more stretching energy and

bear the concentrated stress longer before the cracks propagation to make the films failure.

In contrast, some of Kraton domains almost keeps original shape because the big size domains can not absorb more energy and they are prone to cause cracks grows fast, such as the Kraton D 1116 and Kraton G 1652 in the films made from CHCl_3 . The additions of these big Kraton domains deteriorate the ductility of BPAPC. The shape factor values of these Kraton domains in table 3.3 also proved this point.

4.5 Effect of Annealing

Since the Kraton domain size decreased greatly after the films were annealed around the T_g temperature (150°C) of polycarbonate, we expect the mechanical properties of these polymer blends films can get improvement. But the films after annealing shrank to a very thin and thread – like bar (as shown in Fig. 4.12). We can not test and compare the mechanical properties of this thin bar with the results of the films. So we did not pursue further for the purpose of this thesis.

Fig. 4.12 The shrinking film after annealing at T_g temperature

Reference

- ¹ Rajesh, J.J., Bijwe J., Tewari U.S., *J. Mater. Sci.* **2001**, 36, 351
- ² Hayafure Y., Onozawa, M., Ueki K. *Shikizai Kyokaishi*, **1969**, 42, 357
- ³ Sperling L. H., *Polymeric Multicomponent Materials, an introduction*, **1997**, Ch. 9, p, 259, John Wiley & Sons Inc., New York
- ⁴ van der wal A., Nijhof R., Gaymans R. J., *Polymer*, **1999**, 40, 6031
- ⁵ van der wal A. Verheul A. J. J., Gaymans R. J., *Polymer*, **1999**, 40, 6057
- ⁶ van der wal A. Gaymans R. J., *Polymer*, **1999**, 40, 6067
- ⁷ Jang B.Z., Uhlmann D. R., Vander Sande J. B., *Polymer Engineering and Sci.* **1985**, 25, 643

Chapter V Conclusion and Recommendation for

Future Work

5.1 Conclusion

Blends of Polycarbonate with Kraton D series, prepared from dichloromethane present more delicate and uniform morphology compared with Kraton G series. The average domain sizes of Kraton D series are quite small, especially for the Kraton D 1102 (from 5.5 μm – 15 μm). The domains of Kraton D series exhibit spherical shape before stretching, and they showed elliptical shape on the fracture edge after the films failure. The variations of shape factors of Katon D Series are much greater than Kraton G Series. The blends of Polycarbonate/Kraton D 1102 (at 2 wt %) present the best mechanical properties during the tensile testing.

For the blends of Polycarbonate / Kraton G series, the samples made from dichloromethane have irregular clusters with big Kraton domains, however in the films made from chloroform the Kraton domains presented regular uniform spherical morphology, this morphology change improve the mechanical properties efficiently, such as the Kraton G 1650. But for Kraton G 1652, the oversized spherical Kraton domains formed in BPAPC matrix and this deteriorates the ductility and toughness of BPAPC / Kraton G 1652 films.

The toughening mechanism in the ductile fracture (such as for BPAPC / Kraton D 1102)

is shear yielding dominant, but cavitation of rubber domains is the main mechanism in the other polymer blends. If the Kraton domains sizes are large enough to span more than two cracks surfaces, the films tend to have brittle fractures. So it can be expected that it is an advantage to have several small cavities instead of one large cavity. The improvement or deterioration of mechanical properties of Polycarbonate / Kraton series depends on the multiple reasons, such as Kraton types, solvent effect and Kraton domain size etc.

5.2 Recommendation for Future Work

5.2.1 Suitable Compatibilizer

We attempted to find a suitable compatibilizer to improve the miscibility between the BPAPC and Kratons. Both PMMA and SMA can not work well. But we can imagine if we find an effective one, the morphology of Kraton domains in the polycarbonate could be much more fine and delicate, the Kraton domains sizes would be decreased much, consequently the mechanical properties can be improved greatly, especially for the Kraton G series.

5.2.2 Instron testing with adjustable temperature

We want to study the mechanical properties of BPAPC / Kraton polymer films at high temperature, around the 150 °C, which is the T_g of polycarbonate. We expect that at T_g temperature of polycarbonate, the films might show excellent ductility because the matrix

of films, BPAPC, become more soft and ductile. If we could find a proper instrument to operate this Instron testing under adjustable temperature, we can get new information about the mechanical properties at various temperatures. We can find at what temperature the films fracture behavior change from brittle to ductile. We can get more comprehensive knowledge about the mechanical properties of BPAPC / Kraton blends and this work is absolutely very valuable supplement for our study.

5.2.3 Trials on other Kraton types

We used two types Kratons copolymers in our experiment, Kraton D series (SBS) and Kraton G series (SEBS). But actually styrene-isoprene-styrene (SIS) and styrene-ethylene/propylene (SEP) are also important types of Kratons, which belong to Kraton D and G series respectively. Because the SIS presents more ductile than SBS (the elongation of SIS is ~1500, but SBS is just ~900), we expect the addition of SIS in the BPAPC may improve the elongation of the films more than the SBS types.

APPENDIX

**Tab. A-1 The strength and standard deviation (S.D.) of BPAPC / Kraton
polymer blend films made from CH_2Cl_2 and CHCl_3 at yield and break points**

A. the films made from CH_2Cl_2

Specific sample	Stress at yield (MPa)	S.D. (MPa)	Stress at break (MPa)	S.D. (MPa)
100% PC	57.1	1.4	51.3	1.3
K-1102 2%	49.7	1.9	51.7	1.3
K-1102 5%	43.2	0.4	49.2	0.8
K-1102 10%	37.7	0.8	47.6	0.9
K-1102 15%	36.1	1.3	42.3	1.7
K-1116 2%	46.5	1.1	45.3	0.8
K-1116 5%	39.2	1.0	40.8	1.4
K-1116 10%	34.8	0.4	38.0	0.7
K-1116 15%	30.6	0.9	35.8	0.1

Specific sample	Stress at yield (MPa)	S.D. (MPa)	Stress at break (MPa)	S.D. (MPa)
K-1650 2%	48.5	0.3	45.8	0.8
K-1650 5%	41.9	1.6	42.8	0.3
K-1650 10%	38.9	0.9	39.7	0.9
K-1650 15%	30.2	1.2	34. 0	1.3
K-1652 2%	47.4	0.8	44.8	1.0
K-1652 5%	41.2	1.0	42.2	0.2
K-1652 10%	38.6	1.4	41.7	0.2
K-1652 15%	33.7	1.1	41.1	0.1

B. the films made from CHCl_3

Specific sample	Stress at yield (MPa)	S.D. (MPa)	Stress at break (MPa)	S.D. (MPa)
100% PC	56.4	1.8	55.4	3.4
K-1102 2%	50.7	0.8	64.5	2.5
K-1102 5%	44.1	0.5	42.6	1.2

Specific sample	Stress at yield (MPa)	S.D. (MPa)	Stress at break (MPa)	S.D. (MPa)
K-1102 10%	39.0	0.6	39.9	1.2
K-1102 15%	36.7	0.6	42. 0	0.3
K-1116 2%	47.5	1.5	46.8	0.5
K-1116 5%	40.3	0.4	43.4	0.2
K-1116 10%	32.3	0.9	36.7	0.7
K-1116 15%	28.7	0.4	34.3	0.4
K-1650 2%	47.4	0.7	44.9	1.2
K-1650 5%	42.3	2.1	44.5	1.6
K-1650 10%	34.2	0.8	38.6	0.8
K-1650 15%	29.1	0.2	36.1	0.5
K-1652 2%	55.2	0.4	56.8	0.3
K-1652 5%	46.3	1.1	47.0	1.4
K-1652 10%	36.8	1.0	40.3	0.7
K-1652 15%	33.8	0.7	37.7	0.4

**Tab.A-2 The elongation and standard deviation (S.D.) of the BPAPC / Kraton
films made from CH₂Cl₂ and CHCl₃**

Specific sample	the films made from CH ₂ Cl ₂		the films made from CHCl ₃	
	Elongation (%)	S.D. (%)	Elongation (%)	S.D. (%)
100% PC	29.4	11.2	39.5	14.2
K-1102 2%	102.3	5.5	102.4	1.1
K-1102 5%	74.5	3.6	24.8	12.6
K-1102 10%	74.2	2.0	34.6	10.1
K-1102 15%	53.6	2.6	47.4	4.2
K-1116 2%	34.2	8.3	26.6	0.5
K-1116 5%	27.8	10.1	19.7	3.0
K-1116 10%	24.8	4.2	16.8	1.9
K-1116 15%	28.1	5.0	19.1	1.9
K-1650 2%	12.9	2.4	51.8	9.7
K-1650 5%	41.7	5.4	40.0	1.4
K-1650 10%	16.5	4.7	40.0	2.6

Specific sample	the films made from CH_2Cl_2		the films made from CHCl_3	
	Elongation (%)	S.D. (%)	Elongation (%)	S.D. (%)
K-1650 15%	26.0	1.50	38.8	4.0
K-1652 2%	12.9	1.9	17.0	2.7
K-1652 5%	27.6	8.8	24.4	1.0
K-1652 10%	32.5	9.7	24.7	7.5
K-1652 15%	34.4	5.3	18.8	4.8

**Tab. A-3 The Young's modulus and toughness modulus of the BPAPC / Kraton
films made from CH₂Cl₂ and CHCl₃**

Specific sample	the films made from CH ₂ Cl ₂		the films made from CHCl ₃	
	Young's modulus (MPa)	Toughness modulus (MPa)	Young's modulus (MPa)	Toughness modulus (MPa)
100% PC	1639.5	30.1	1926.6	28.1
K-1102 2%	1450.0	47.2	1531.2	49.5
K-1102 5%	1246.4	32.2	1272.0	27.3
K-1102 10%	1153.3	27.5	1158.7	18.2
K-1102 15%	1053.6	22.9	978.9	15.9
K-1116 2%	1527.2	17.7	1516.6	11.4
K-1116 5%	1261.1	14.9	1472.0	8.6
K-1116 10%	1037.9	9.3	1398.0	5.4
K-1116 15%	890.6	8.0	1170.6	4.8
K-1650 2%	1605.5	5.4	1455.6	19.5

Specific sample	the films made from CH_2Cl_2		the films made from CHCl_3	
	Young's modulus (MPa)	Toughness modulus (MPa)	Young's modulus (MPa)	Toughness modulus (MPa)
K-1650 5%	1379.3	14.9	1326.8	21.4
K-1650 10%	1168.0	7.4	1194.8	13.9
K-1650 15%	996.0	7.0	1034.2	11.4
K-1652 2%	1767.2	5.7	1873.0	8.1
K-1652 5%	1513.2	10.9	1332.7	9.7
K-1652 10%	1201.0	11.3	1228.8	8.7
K-1652 15%	1042.0	12.8	1005.6	4.4

Tab. A-4 The resilience modulus and abrasion resistance of the BPAPC /

Kraton films made from CH₂Cl₂ and CHCl₃

Specific sample	the films made from CH ₂ Cl ₂		the films made from CHCl ₃	
	Resilience modulus (MPa)	Abrasion Resistance (KPa)	Resilience modulus (MPa)	Abrasion Resistance (KPa)
100% PC	1.7	7.9	1.2	4.3
K-1102 2%	1.0	8.2	1.5	12.4
K-1102 5%	1.1	7.3	1.5	7.9
K-1102 10%	0.8	4.9	1.1	4.1
K-1102 15%	0.9	5.0	1.0	4.1
K-1116 2%	1.2	3.3	1.1	2.1
K-1116 5%	0.8	2.3	0.9	1.3
K-1116 10%	0.7	1.5	0.5	0.4
K-1116 15%	0.6	1.3	0.4	0.4
K-1650 2%	0.9	0.8	1.1	3.8

Specific sample	the films made from CH ₂ Cl ₂		the films made from CHCl ₃	
	Resilience modulus (MPa)	Abrasion Resistance (KPa)	Resilience modulus (MPa)	Abrasion Resistance (KPa)
K-1650 5%	1.0	2.8	1.0	4.1
K-1650 10%	1.2	1.8	0.7	2.0
K-1650 15%	0.7	1.3	0.6	1.6
K-1652 2%	0.9	0.8	1.2	1.3
K-1652 5%	0.8	1.5	1.2	2.2
K-1652 10%	1.0	2.4	0.9	1.5
K-1652 15%	0.9	2.8	0.7	0.8

**Fig. A – 1 domain size distribution of Kraton D 1102 10% and 15% in the films
 made from CH_2Cl_2 and CHCl_3**