RUBBER TOUGHENING OF PHENOLIC RESIN BY USING NITRILE RUBBER AND AMINO SILANE

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Approval of the Graduate School of Natural and Applied Sciences

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ABSTRACT

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The aim of this study was to investigate rubber toughening of resol type phenol-formaldehyde resin. For this purpose, phenolic resin was first modified by only acrylonitrile butadiene rubber, and then by using nitrile rubber together with 3-aminopropyltriethoxysilane.

Test specimens were prepared by mixing and casting of liquid phenolic resin in three groups. In the first one, neat phenolic resin specimens were produced. In the second group, phenolic resin was modified with 0.5, 1, 2, and 3 wt.% nitrile rubber, while in the last group modification was carried out by using 0.5 wt.% nitrile rubber together with 1, 2, and 4 wt.% amino silane (with respect to nitrile rubber). All specimens were heat cured in the oven.

In order to observe behaviors of the specimens, Three-Point Bending, Charpy Impact, Plane-Strain Fracture Toughness, and Dynamic Mechanical Analysis tests were conducted according to the related ISO standards for all specimens groups. Scanning Electron Microscopy (SEM) was also used for the fractographic analysis of some samples.

It is concluded that, although there were problems in mixing and casting of liquid resol type phenolic resin, its toughness could be improved by using nitrile rubber and amino silane. Modification by using nitrile rubber and amino silane together was much more effective than by using only nitrile rubber. In this synergistic case for instance, Charpy impact strength and fracture toughness values of the neat phenolic specimens were increased 63% and 50%, respectively. SEM studies indicated that the main rubber toughening mechanism was shear yielding observed as deformation lines especially initiated at the domains of nitrile rubber and amino silane.

Keywords : Rubber toughening, resol type phenol formaldehyde resin, acrylonitrile-butadiene rubber, 3-aminopropyltriethoxysilane, mechanical properties, thermal properties, SEM fractography

ÖZ

FENOLİK REÇİNENİN NİTRİL KAUÇUK VE AMİNO SİLAN KULLANARAK KAUÇUK TOKLAŞTIRILMASI

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Bu çalışmanın amacı resol türü fenol formaldehit reçinenin kauçuk toklaştırılmasının incelenmesidir. Bu amaçla, fenolik reçine ilk önce akrilonitril-bütadien kauçuğu tek başına, daha sonra ise 3-aminopropiltrietoksisilan ile birlikte kullanarak modifiye edilmiştir.

Test numuneleri sıvı fenolik reçinenin karıştırılıp dökülmesiyle üç farklı grupta hazırlanmıştır. Birinci grupta, saf fenolik reçine numuneleri üretilmiştir. İkinci grupta, fenolik reçine, 0.5, 1, 2, ve 3 ağr. %'li nitril kauçukla modifiye edilirken, son grupta ise, modifikasyon, 0.5 ağr.%'li nitril kauçukla birlikte onun miktarının 1, 2, ve 4 ağr. %'li amino silanla birlikte kullanılarak yapılmıştır. Tüm numunelerin kür işlemi fırında ısıyla yapılmıştır.

Numunelerin davranışlarını incelemek için, Üç Noktalı Eğme, Charpy Darbe, Düzlem-Gerinimli Kırılma Tokluğu ve Dinamik Mekaniksel Analiz testleri, ilgili ISO standartlarına göre tüm numune grupları için uygulanmıştır. Aynı zamanda, bazı örneklerin kırılma yüzeyleri Taramalı Elektron Mikroskobu ile incelenmiştir.

Sonuç olarak, resol türü sıvı fenolik reçinenin karıştırılıp dökülmesiyle ilgili sorunlar olmasına rağmen, fenolik reçinenin tokluğu nitril kauçuk ve amino silan kullanılarak artırılabilmektedir. Nitril kauçuğu amino silanla birlikte kullanarak yapılan modifikasyon, sadece nitril kauçuk kullanarak yapılandan çok daha etkili olmuştur. Bu sinerjistik durumda örneğin, saf fenolik reçine numunelerinin Charpy Darbe Dayanımı ve Kırılma Tokluğu değerleri sırasıyla 63% ve 50% oranında artmıştır. SEM çalışmaları ana kauçuk toklaştırma mekanizmasının özellikle nitril kauçuk ve amino silan fazlarından başlayan deformasyon çizgileri şeklinde gözlemlenen kesme akması olduğunu göstermiştir.

Anahtar Sözcükler: Kauçuk toklaştırması, resol türü fenol-formaldehit
reçine, akrilonitril-bütadien kauçuk,
3-aminopropiltrietoksisilan, mekaniksel özellikler,
ısıl özellikler, SEM analizi

TO MY FAMILY AND SIMLA

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INTRODUCTION

Phenolic resins are one of the oldest commercial polymeric resin systems and identified with the beginning of the plastic industry. Although resinous products based on phenol and formaldehyde have been known since 1872, Leo Baekeland was able to develop in 1907 an economical method to convert these resins to moldable formulations. Phenolic resin has many desirable properties such as good dimensional stability, lower system cost, good heat and chemical resistance. The most important property, however, that differentiates phenolics from other plastic composites is excellent creep resistance at high temperatures [1].

Consequently, they are widely used for many important applications, such as insulating material for electric components, structural adhesives, reinforced plastics and matrix resins for advanced composite materials. However, its high brittleness due to the higher crosslinking density and cure shrinkage are the major drawbacks that hinder the widespread applications of phenolic resins. These problems can be overcome by the usage of elastomeric additives such as rubber. Therefore, in this study, rubber toughening of a resol type phenolic resin will be investigated by using a nitrile rubber and a silane. First, some theoretical review and literature survey will be given in the following sections.

1.1 Phenolic Resins

Phenolic resins are usually considered as the condensation products of phenol with formaldehyde. Although the most frequently used aldehyde is the formaldehyde, others, like furfural may also be applied to produce resins having good molding properties. Similarly, other phenols, such as cresols, butyl phenol and resorcinol may be also used instead of phenol to get special properties. Phenol and formaldehyde constitute almost 75 and 90% of all present phenolic resin production [2].

Condensation reaction between phenol and formaldehyde is not a simple one and the products obtained depend very much on the type of catalyst used, the relative proportions of the reactants and the time of reaction. The (unmodified) phenol-formaldehyde resins exhibit high dimensional stability over a wide temperature range; 180 to 200ºC for long periods of time [3]. They exhibit good thermal and chemical resistance with a low flammability and a low smoke density. They are insoluble in most hydrocarbons and highly resistant to moisture absorption.

According to type of catalyst and mole ratio of the reactants, phenol-formaldehyde resins are of two main types: novolacs and resols. Novolac resins can be prepared by the reaction of an excess of phenol with formaldehyde under acidic conditions, whereas resols are prepared by the reaction of phenol with excess formaldehyde under basic conditions. General properties of these two types of phenol-formaldehyde resins are given in Appendix A.

1.1.1. Novolacs

Novolacs or two-step resins are low molecular weight, fusible but insoluble prepolymers prepared by reacting less than one mole of formaldehyde with phenol in the presence of acid catalysts such as formic, sulfuric, phosphoric acids. They have an outstanding property profile and are one of the least costly compounds available. However, splitting out of ammonia during processing is their chief drawback. Novolacs can be used frequently as molding compounds, coated foundry sand and brake-lining binders. Structural formula of novolacs is given in Figure 1.1

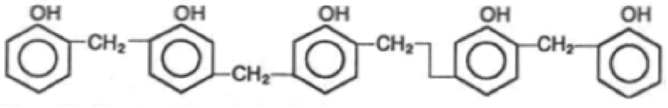


Figure 1.1 Structural formula of novolac resins

1.1.2 Resols

In many cases, resol type phenol-formaldehyde resin is liquid and has a low to medium molecular weight [4]. It is usually in a solution of alcohol or an aqueous dispersion which provide a high degree of formulation flexibility. In the formation of resols, phenol and excess formaldehyde react to produce a mixture of methylol phenols in the ortho and para position (Figure 1.2).

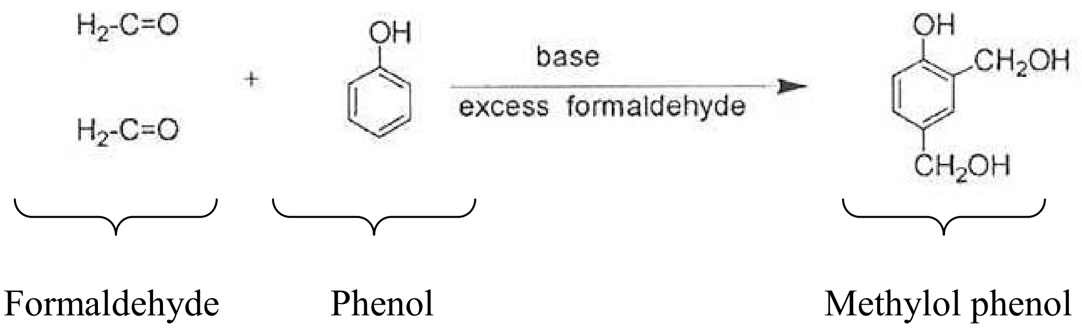


Figure 1.2 Formation of methylol phenol

The hydroxymethyl groups on these compounds can condense with unreacted but active positions on other phenolic rings (Figure 1.3 (a)), or hydroxymethyl groups on different phenolic rings can condense together (Figure 1.3 (b)).

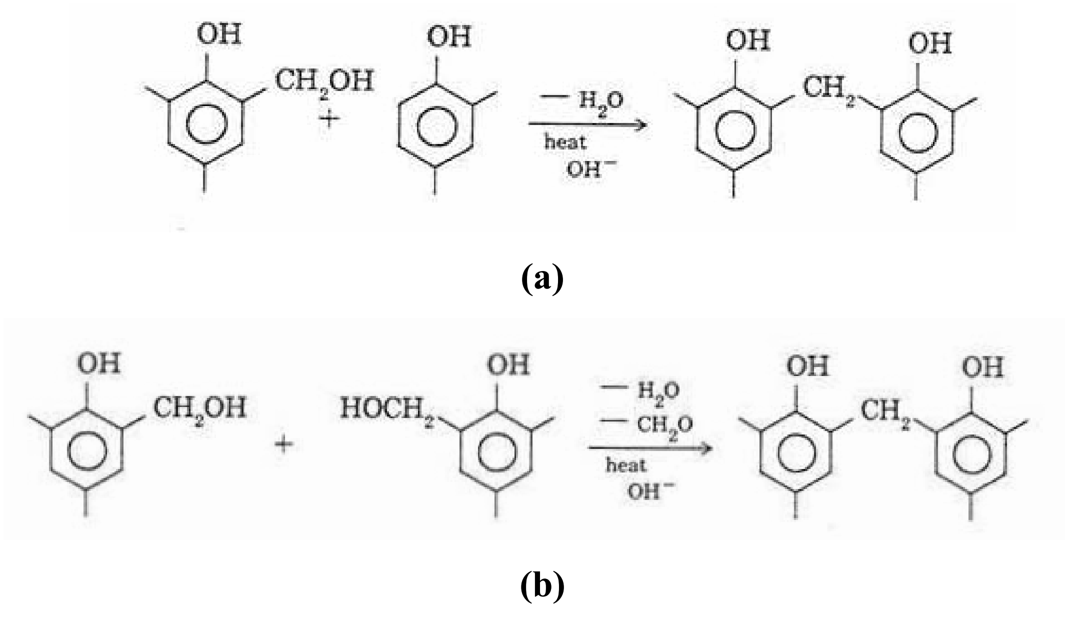


Figure 1.3 Two different reactions for the formation of resol type resins

In either case a methylene bridge forms between aromatic rings [5]. Thus, in the structure of a typical resol, both methylene bridges and methylol groups are present.

Resol type phenol-formaldehyde resins do not outgas ammonia during the process as do the novolac compounds. Thus, the resol compounds are used for applications where their lack of out gassing is most beneficial and essential. They are used for odor-free applications such as closures, refrigerator controls, electrical devices, pumps and vaporizers. The main disadvantage of this type of product is their sensitivity to temperature [3]. This makes it imperative to produce these compounds in air-conditioned rooms and to store the finished goods in similar conditions.

1.1.3 Curing Behaviors of Phenolic Resins

One of the significant properties of the phenolic resins is their ability to transform from the liquid state to the solid state by forming covalently bonded three dimensional network structure. This process called curing or hardening is done by the addition of an acid or by the application of heat.

The crosslinking of phenol and formaldehyde is a polycondensation reaction [6]. During the reaction, the by-product water is produced and because of the difficulty of its elimination, all commercial phenol-formaldehyde resins contain water. Through the crosslinking, they can undergo following morphological stages.

Stage A : Beginning stage, resin is liquid, meltable and solvable
Stage B : Middle stage, crosslinking is commenced and the resin is thermoplastic, unmeltable, unsolvable
Stage C : End stage, resin is completely thermoset, unmeltable, unsolvable

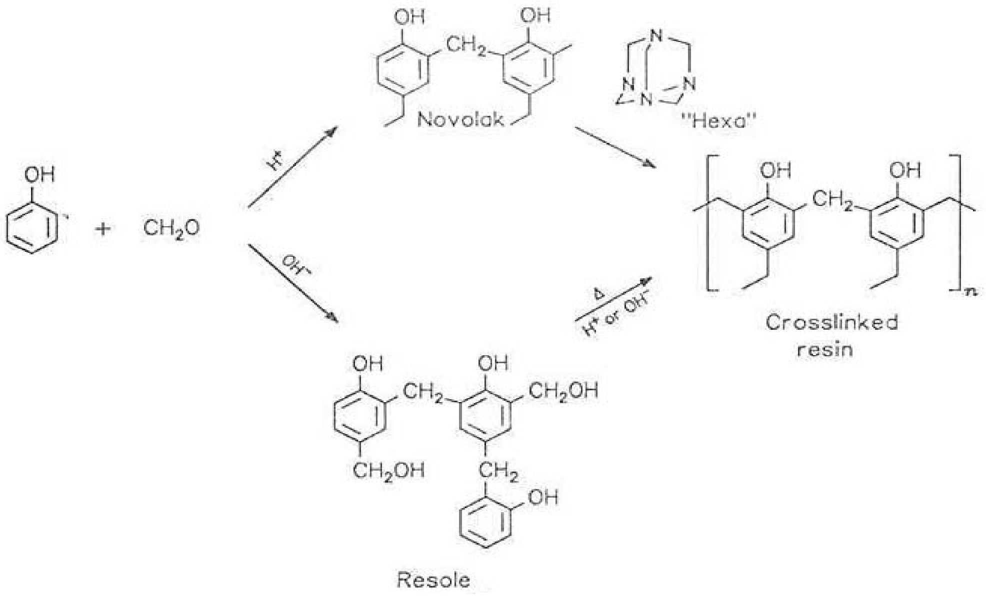


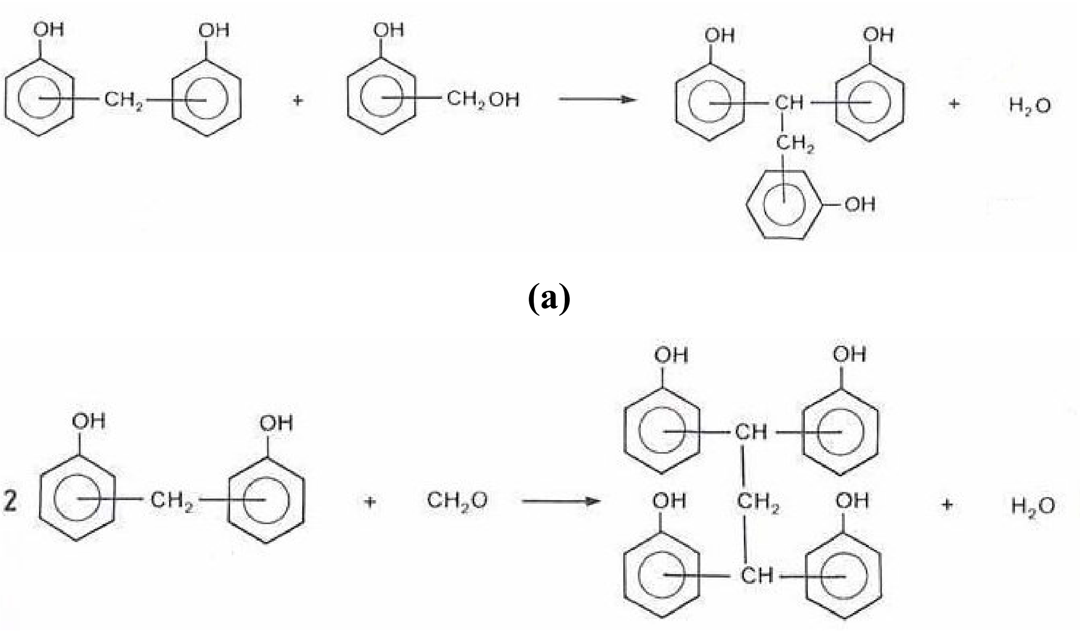
Figure 1.4 Curing Scheme of Phenol-Formaldehyde resins

(i) Curing of Novolacs

Novolacs require a source of formaldehyde for the transformation into a crosslinked resin. The additional formaldehyde can be in the form of paraform or an oligomer of formaldehyde that composes to formaldehyde upon heating. This additional formaldehyde can also be supplied from hexamethylenetetramine (hexa)[7]. Hexa is the reaction product of ammonia and formaldehyde, which decomposes back to formaldehyde and ammonia upon heating and provides methylene groups, -CH_2-, which crosslinks the resin and transforms it into a thermoset. In addition to water, novolacs can also split out of ammonia as a reaction by-product.

(ii) Curing of Resols

Several curing options are available in resol type phenol-formaldehyde resins. Mostly, resols can be cured thermally with no catalyst addition. Heat curing is conducted at temperatures below 100ºC to avoid boiling the water that would be condensed during the curing reaction [8]. As the curing proceeds, many reactions take place simultaneously in the resol type phenol-formaldehyde system. Such as the condensation of methylene bridge with hydroxymethyl group (Figure 1.5 (a)) and crosslinking of methylene bridge with formaldehyde (Figure 1.5 (b)) [9].



(a)

(b)

Figure 1.5 Two reactions that may take place during curing of resols

Since this is a polycondensation reaction, the molecular weight increases with conversion. However, as the molecular weight increases, the water already present in the resin and that produced during the reaction becomes incompatible with the curing resin and phase separates to produce water domains. These are observed as 'microvoids' 2-10 μm in diameter in the cured matrix. The size of these domains is governed by the surface tension of the resin, the rate and extent of the curing reaction [10].

1.2 Toughening of Polymers

In the engineering applications, it is important to characterize the mechanical properties of materials. By the application of mechanical force to the specimen, deformed material will be analyzed by its stress-strain behavior. This behavior quantifies the stress (load) required to achieve a certain amount of strain (deformation). Figure 1.6 shows typical stress-strain curve of a ductile polymer.

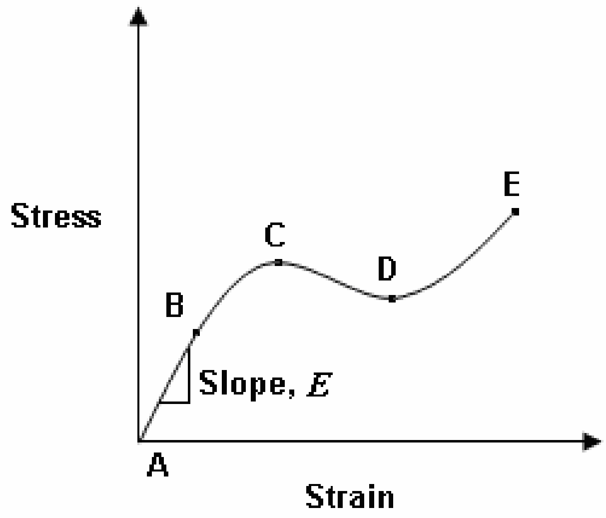


Figure 1.6 Stress-Strain Curve of a Ductile Polymeric Material

Between A and B, Hooke's law for an elastic solid is followed, so that the initial slope stands for the modulus of rigidity, *E*. The point C represents the yield point, which is considered the upper limit of elasticity. From this point on, plastic response prevails which is an irreversible process. In the region C-D, a decrease of stress is observed which is caused by the formation of a neck (cross-section drops suddenly in the center) in the specimen. The last portion of the stress-strain curve indicates strain hardening induced mainly by further chain orientation. At the point E fracture occurs and the ultimate elongation is reached.

Very brittle polymeric materials show a different stress-strain behavior. They typically end abruptly (suddenly) in fracture after a small amount of linear elastic deformation. Figure 1.7 shows this behavior.

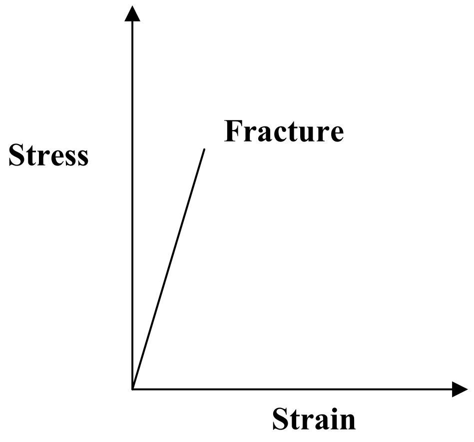


Figure 1.7 Stress-Strain Curve of a Brittle Polymeric Material

The toughness of a specimen refers to the total amount of energy required to cause fracture. In a broader sense, it is a measure of material's resistance to failure. Depending on the application, toughness is usually measured as either area under the tensile stress-strain curve, the Izod impact strength, the Charpy impact strength or the plane-strain critical stress intensity factor (K_{IC}). For example, the polymeric material whose stress-strain behavior is shown in Figure 1.6 has more energy absorption (toughness) than the polymeric material in Figure 1.7.

Toughness is usually highly desirable. It can only be defined precisely under a given set of test conditions. There are many factors which affect the toughness of polymeric materials:

- Chemical crosslinks
- Effects of anisotropy (chain orientation)
- Effects of temperature and deformation rate during testing
- Effects of the mode of deformation
- Effects of variations in the specimen geometry (thick specimens are more likely to fail in a brittle manner)
- Effects of factors related to the fabrication parameters or end-use conditions.

There are mainly three basic mechanisms available for the energy absorption of a polymeric material under load: “shear yielding”, “crazing” and “cracking”.

Shear yielding is the irreversible change of shape of the material under stress. It may occur over the entire stressed region of material or it may occur in localized portion of the material, in which case it is usually referred to the response as shear “banding” [11]. Shear yielding is mostly observed in ductile polymers like nylon or polycarbonate. However, it can also be seen in crosslinked materials like epoxy.

Crazing is a localized irreversible volume expansion. It is often seen in tensile experiments as optical discontinuities that resemble cracks. A craze is initially less dangerous than a crack because at least some load can be transmitted across it. However, at some critical point, a craze will degenerate into crack – the voids coalesce – if the load is held constant or increased. Crazing is highly successful toughening mechanism for vinyl polymers like polystyrene [12]. In order for the mechanism to be successful, however, large number of crazes must be generated.

Cracking will normally follow shear yielding and/or crazing. However, at sufficiently low temperatures neither shear yielding nor crazing will occur and only crack formation will be available. Of the three, crazing and shear yielding offer much higher energy absorption potential and are consequently to be preferred. This higher potential arises because large numbers of shear bands or crazes be activated under stress, while only a few crack planes are normally found at failure.

1.2.1 Toughening of Thermosets

Thermosets exhibit individual chains that are chemically crosslinked by covalent bonds during polymerization, which give rise to a final three-dimensional network. These covalently bonded crosslinked structure leads to good creep resistance and improved heat resistance for all thermosets. However, having long processing times and brittle character due to their crosslinks are the major drawbacks of these materials.

The commonly known approaches for toughening brittle thermosets include; chemical modification of a given rigid thermoset backbone to a more flexible backbone structure, increase of thermoset molecular weight, lowering of the crosslink density of the cured resin via use of low functionality curing agents and incorporation of dispersed toughener phase (rubbery and/or thermoplastic) in the thermosetting matrix [25].

Although, among these approaches, toughening via dispersed elastomeric phase (rubber) has been shown to be the most effective and can provide an order of magnitude toughness improvement, its basic limitation is that increase in toughness can be achieved only at the expense of high-temperature performance or of mechanical properties (a decrease in modulus and strength). This can not be tolerable for the long-term and structural applications. Other limitation of rubber toughening is the lack of significant success in the toughening of high-T_g networks.

To overcome these drawbacks, semi-crystalline thermoplastics can be used instead of rubber particles [26]. Thus, an increasing toughness value can be obtained without any loss in stiffness and thermal properties. For this purpose, either thermoplastic powders (like polyamid or polybutyleneterephtalate) or initially miscible thermoplastics (like polyetherimide or polysulfone) can be incorporated to the thermosetting matrix. Initially miscible thermoplastics may be separated in the course of polymerization and may use to toughen moderately high T_g networks. The main problem arising from these miscible particles is the controlling of morphologies. By the use of preformed nonmiscible thermoplastic powders, morphologies and thermal properties of the material can be easily controlled and designed. Main drawback with these materials is the high viscosity of the initial dispersions and the possibility of producing agglomeration of particles during processing.

Although, either of these dispersed toughener phases (rubber or thermoplastic) has been used to modify the thermosetting matrix, both of them can also be applied to the material. Thus, T_g and modulus reductions resulting from the usage of rubber particles can be improved by the thermoplastics incorporated into the matrix material. Woo *et al.* [27] studied an epoxy system with both thermoplastic (polysulfone) and rubber particles (carboxyl terminated butadiene acrylonitrile). They concluded that limited toughness improvement was achieved for the epoxy system modified with only thermoplastic or the rubber by itself. However, when a proper combination of both the rubber and thermoplastic was incorporated into the epoxy matrix, a significant increase in fracture toughness value without any T_g and modulus depression was observed.

1.2.2 Rubber Toughening of Thermosets

Athough rubber toughening is generally used for thermoplastics including polystyrene [13,14], Nylon 6,6 [15,16], polymethyl-methacrylate [17,18], polyvinylchloride [19] and polypropylene [20,21], it is also applied to thermosets for instance epoxy [22-24].

Thermosets can be toughened by rubber particles with mainly two different morphologies which are either the usage of “core-shell rubber particles” or initially “miscible reactive rubbers”. Core-shell rubber particles are prepared by emulsion polymerization and exhibit alternating rubbery and glassy layers. These particles have been used to modify thermosets, such as epoxies, cyanates, vinyl ester resins. A particle consists of a rubbery core and an outer shell of a glassy polymer. The rubbery core is generally based on polybutadiene. The outer glassy shell is required to prevent coalescence of rubbery particles during synthesis, and to insure a good interface with the matrix. The shell is usually based on styrene/ acrylonitrile copolymers. The main problem resulting form the usage of core-shell toughening is obtaining a good dispersion. A good dispersion increases the particle surface contact with the matrix, producing a considerable increase in viscosity [26].

However, the most widely used method for the rubber toughening is the addition of initially miscible rubbers into the thermosetting matrix. Depending upon the type of rubber and thermosetting material used, the rubber may form a secondary phase during the polymerization (curing) reaction. The degree to which this phase separation occurs can control not only the amount of toughening obtained, but also a number of other properties such as the glass transition temperature and the modulus of the system [28].

For a given volume fraction of the rubbery phase, there is a critical particle size below which toughening occurs and above which there is no significant effect. To find out this critical size, Van der Sanden [29] and Wu [30] defined a new parameter called critical interparticle distance for thermosets and for thermoplastics respectively. Their parameters were independent of rubber volume fraction and particle size and are characteristic of the matrix material. According to these authors, when the average interparticle distance is smaller than the critical value, a system is tough otherwise is brittle.

When failure occurs in thermoset systems, usually more than one toughening mechanism is taking place. Therefore, it is important to first consider the most effective toughening mechanism like “shear yielding” and then promote other effective minor toughening mechanisms.

In the mechanism of “shear yielding” as it is mentioned in Section 1.2, rubber particles initiate shear bands or deformation zones by causing stress concentration at the surrounding matrix (Figure 1.8). Thus, if many particles are present, the toughness will be improved because more deformation zones will be created before fracture.

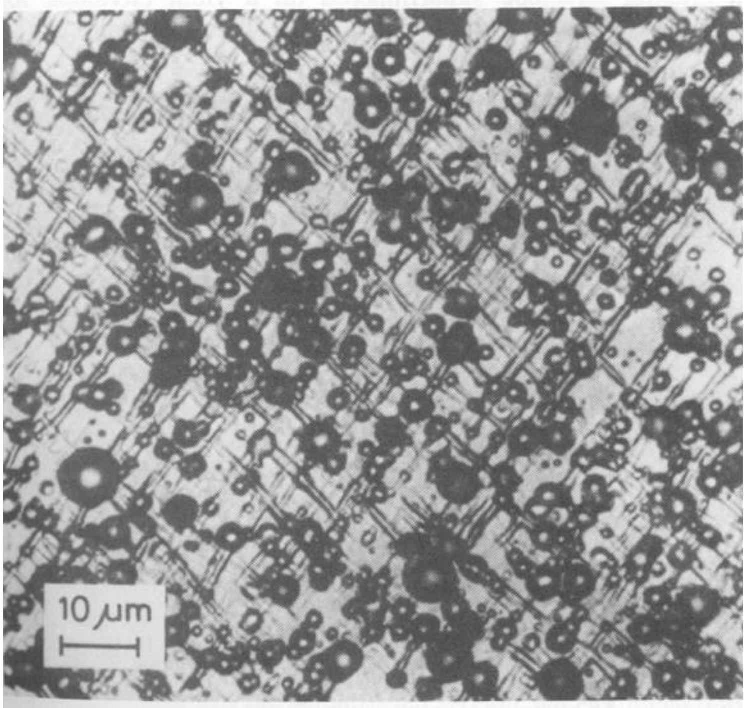


Figure 1.8 Shear Bands or Deformation Zones formed in the Matrix [25]

In addition to shear yielding, some other toughening mechanisms such as "microcracking", "crack deflection", "crack bifurcation", "crack pinning", "crack bridging" or "multilevel fracture path" (enlargement of fracture surface area) can be also operative. However, these mechanisms are less effective than the "shear yielding" mechanism and relatively low in energy absorption capacity.

For the *microcracking* mechanism to take place, the interfacial adhesion between the matrix and the toughener phase does not need to be strong. Debonding at the interface and microcracking can effectively serve the purpose of shielding the crack and impeding crack growth [25].

For the *crack deflection* and *crack bifurcation* mechanisms to occur, the toughener phase needs to produce sufficient stress field in front of the growing crack. Thus, this stress field can alter the path of the crack growth and bifurcation and deflection mechanisms can take place in the matrix. Besides, rubber particle (or a hole) size also plays an important role in deflecting the crack. Larger particles can deflect the crack path easily than the smaller ones (Figure 1.9) [25].

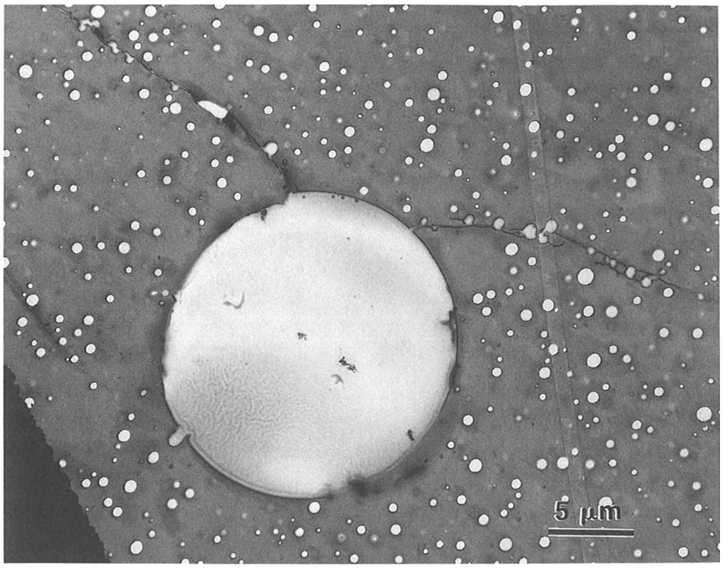


Figure 1.9 A Large Particle Deflecting the Crack Path [25]

In the mechanism of *crack pinning*, particles act as obstacles for the crack front. When the crack propagates between particles, it has to bow locally (Figure 1.10) [26] and require more energy to grow. The crack pinning mechanism needs that the rubber particles must adhere to the matrix strongly.

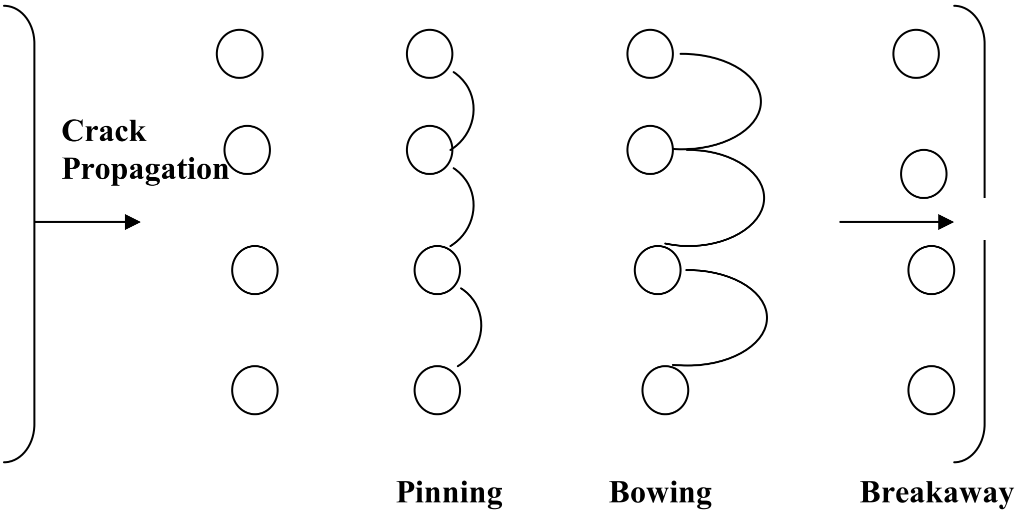


Figure 1.10 Scheme of the Crack Pinning Mechanism

Crack bridging mechanism is illustrated in Figure 1.11 [26]. Particles are stretched from their edges by the propagating crack and promote to increasing of fracture energy. This mechanism again, as in the case of crack pinning, needs a good adhesion between the matrix and particles. However, because of the very low modulus of rubber particles, dissipated energy in such a mechanism is low.

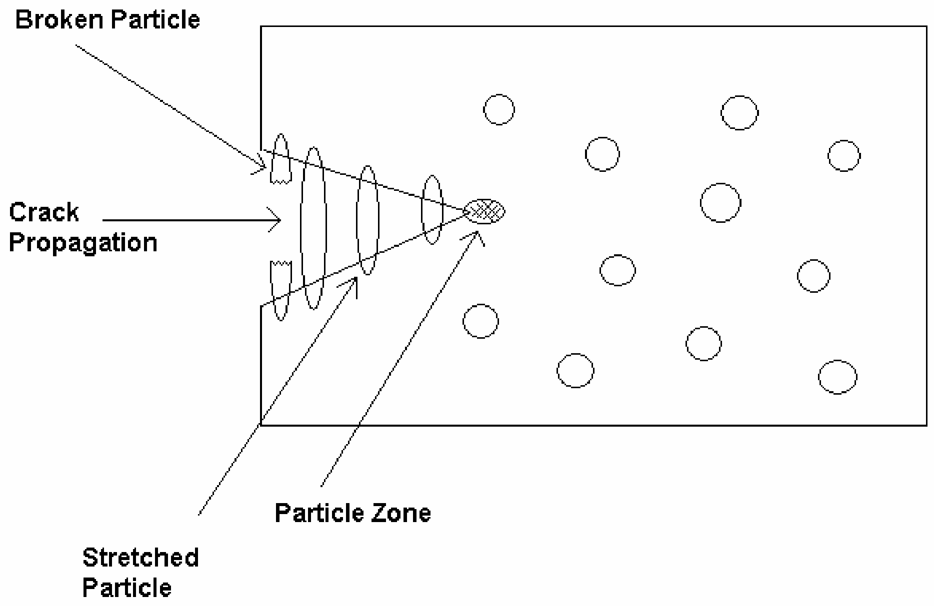


Figure 1.11 Illustration of Crack Bridging Mechanism [26]

1.2.3 Use of Silanes in Rubber Toughening

Organosilicon compounds were first developed as coupling agents in composite industry 60 years ago. By the usage of these materials, it is possible to bring about dissimilar materials such as organic polymer and inorganic substrate. They are capable of reacting with and forming covalent chemical bonds with phases present in the structure.

They have the general structure R-Si $(OR^1)_3$, where R is an organo-functional group selected for bonding to organic polymers while (OR^1) is a hydrolysable group. In this study, the usage of organosilane compounds are quite different from their conventional usage i.e., as coupling agents. They form spherical domains like rubber particles in the phenolic matrix and contribute to the shear yielding and/or other energy absorption mechanisms.

In silane treatment applications, the alkoxy groups of trialkoxysilanes are hydrolyzed to form silanol containing species. They are highly reactive intermediates and can react with each other to form a condensation product as shown below:

Hydrolysis

$$\mathrm{R\text{-}Si(OR^1)_3 + 3H_20 \rightarrow R\text{-}Si(OH)_3 + 3R^1OH}$$

Condensation

$$\mathrm{R\text{-}Si(OH)_3 + R\text{-}Si(OH)_3 \rightarrow R\text{-}Si(OH)_2OSi(OH)_2\text{-}R + H_2O}$$

Thus, at the end of the condensation reaction, polyorganosiloxanes can form. They are generally prepared by reacting chlorosilanes with water to give hydroxyl compounds which then condense to give polymer structure (silicone elastomers) [31]. Similar reactions can also be written for alkoxysilanes.

1.3 Previous Works on Rubber Toughening of Thermosets

The first serious attempt to explain the question of how an immobile, crosslinked glassy thermoset be toughened by rubber particles was made by Kunz and Douglass [32]. They developed a model which was based upon the energy dissipation during stretching and bridging of the crack surfaces by rubber particles. However, it is now generally accepted that rubber bridging mechanism only plays a secondary role in the toughening of brittle thermosets.

Sultan and McGarry [33] were the first to use the concept of rubber toughening in a thermosetting matrix; epoxy. In their study, they used carboxyl-terminated acrylonitrile (CTBN) liquid rubber to toughen diglycidyl ether of bisphenol A (DGEBA) epoxy resin. They pointed out that toughening depends on the rubber particle size; 40 nm particles being not as efficient as 1μm particles. Their study showed that nearly five-fold of increase in fracture energy values was observed when large particles (1μm) were used instead of small ones (40nm).

Pearson and Yee [34] tried to investigate the rubber particle size dependence on toughening mechanisms. They prepared an epoxy system (DGEBA) with liquid reactive rubber (CTBN). Eventually, they concluded that relatively large particles (100-200 μm) provided only a modest increase in fracture toughness by a particle bridging/crack deflection mechanism. In contrast, smaller particles provided a significant increase (%90) in toughness by shear banding mechanism.

Frounchi *et.al.* [22] carried out experiments by adding solid acrylonitrile-butadiene rubbers (NBR) to DGEBA type epoxy resin. Their study showed that increasing the acrylonitrile content of the rubber (from 19 to 33%) caused better compatibility between NBR and epoxy resin. Thus, they obtained effective toughening and 40% increase in impact resistance.

Kaynak *et.al.* [35-39] investigated rubber toughening of DGEBA type epoxy resin by using various modifiers such as; a reactive rubber (HTPB), a silane coupling agent (SCA), recycled scrap tire rubber particles, a liquid elastomer (Tegomer). They used these modifiers separately and with various combinations. They also studied effects of mixing order during specimen preparation, and surface modification of these rubber particles. They indicated that toughness of the brittle epoxy can be improved much effectively when these modifiers were used at certain synergistic combinations with certain surface treatments.

Chen and Jan [40] prepared a bimodal distributed liquid rubber particles (CTBN) in epoxy resin (DGEBA) and studied the fracture behavior of the system. They eventually found out that a 171% increase in fracture energy was obtained when the bimodal rubber particles were utilized instead of using unimodal ones. However, this was not the case in the work of Pearson and Yee [34]. They examined the bimodal mixtures of epoxies containing small and large particles. But, they did not observe any significant improvement in fracture energy.

Geisler and Kelley [41] used a combination of alumina and core-shell rubber particles with epoxy matrix in order to balance some of the drawbacks produced by rubber toughening (decrease in modulus and high temperature performance). In their study, it was observed that cured epoxy system having rubber and alumina particles had fracture toughness values 25% higher than those of epoxy systems having only rubber or alumina particles. They also indicated that toughness improvement do not lead to any decrease in T_g and modulus.

In addition to these studies, Yee and Pearson [42] also analyzed the effect of matrix T_g on rubber toughening. They demonstrated that the low crosslink density epoxies were far more readily toughened than the high crosslink density ones.

1.4 Aim of This Study

As presented in the previous sections, rubber toughening in many thermosetting materials is well established. However, this is not the case for phenolics, especially for resol type phenolic resins. This could be mainly due to the curing difficulties during specimen production by casting. Curing in resol type phenolic resins should be conducted at temperatures below 100 ºC to avoid boiling of water (a by product of the curing reaction) leading to very long curing times (2 or 3 days at 80 º C). Otherwise, water evaporation will lead to bubble formation and densely voided structure.

Therefore, the aim of this study was to investigate the effectiveness of rubber toughening of resol type phenol-formaldehyde resin by using acrylonitrile butadiene rubber. In order to observe the possibility of synergistic effects of silanes, 3-aminopropyltriethoxysilane was also used.

CHAPTER II

EXPERIMENTAL WORK

2.1 Materials

Thermosetting matrix material used in this work was a phenolic resin. For toughening purposes, a nitrile rubber and an amino silane were used.

2.1.1 Phenolic Resin

As the phenolic resin, resol type phenol-formaldehyde was chosen. This resin in liquid form was supplied from Borden Chemicals (USA). Some physical properties of the resin are given in Table 2.1

Table 2.1 Physical Properties of Resol type Phenol-Formaldehyde Resin

Property	Unit	Value
Viscosity (at 25°C)	cps	180-300
Solids (at 135°C)	%	60-64
pH (at 25°C)	-	7.9-8.5
Gel Time (at 135°C)	min	11-18
Specific Gravity	-	1.070-1.100
Solvent	-	Isopropyl Alcohol

2.1.2 Nitrile Rubber

Powder rubber particles used for toughening were the acrylonitrile-butadiene rubber (NBR) which was supplied from Bayer (Germany). Some specified properties of this product are given in Table 2.2. Figure 2.1 shows its chemical structure.

Table 2.2 Specified Properties of NBR

Property	Unit	Value
Mooney Viscosity ML 1+4, 100°C	-	45 ± 5
Density (at 23°C)	g/cm^3	0.98
Particle Size	mm	0.7
Volatiles	%	≤ 0.5
Ash Content	%	1.1 ± 0.3
Bound ACN content	%	33 ± 1

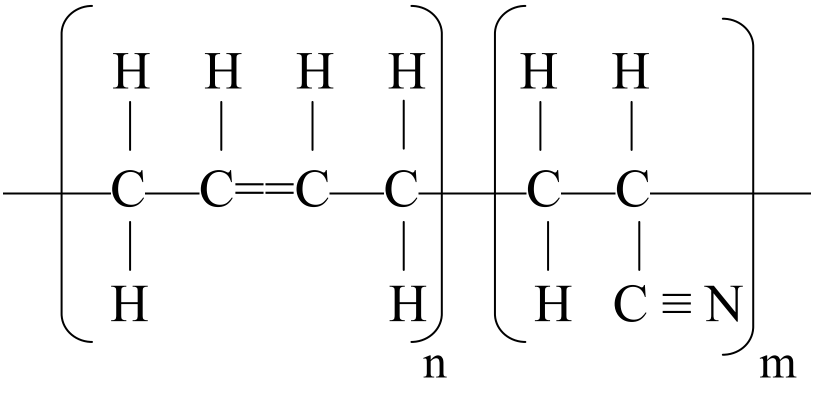


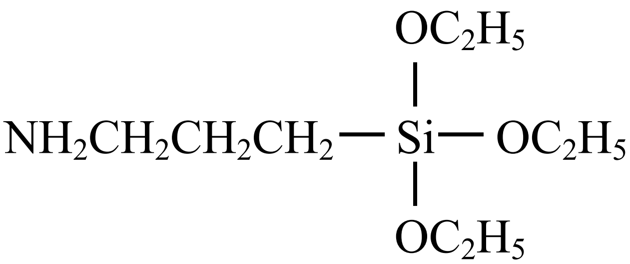
Figure 2.1 Chemical Structure of NBR

2.1.3 Amino Silane

For the synergistic effect in rubber toughening, together with nitrile rubber particles, an amino silane was also used. It was 3-aminopropyltriethoxysilane, a product of Degussa (Germany). The chemical structure of this product is given in Figure 2.2. Some of its physical properties are given in Table 2.3

Table 2.3 Some Physical Properties of 3-aminopropyltriethoxysilane

Property	Value	Unit
Density (20 °C)	0.95	g/cm^3
Refractive Index (n)	1.422	-
Boiling Point (4 hPa)	>68 °C	°C
Flash Point	93 °C	°C
Viscosity (20 °C)	1.85	mPa.s



$$NH_2CH_2CH_2CH_2-\overset{\overset{OC_2H_5}{|}}{\underset{\underset{OC_2H_5}{|}}{Si}}-OC_2H_5$$

Figure 2.2 Chemical Structure of 3-aminopropyltriethoxysilane

2.2 Production of the Specimens

In this study, specimens were produced in three main groups. In the first group, only neat phenolic resin was used. In the second group phenolic matrix was modified with nitrile rubber particles, and in the final group modification was carried out both with nitrile rubber and amino silane. Production scheme of these three main groups are given in Figure 2.3.

2.2.1 Mixing and Molding

(i) Group I Specimens: In the production of neat phenolic specimens, first resin was taken from refrigerator and put onto a hotplate. Then, it was mechanically mixed (40 rpm) at 35ºC for 1 hour in order to decrease its viscosity. Finally, resin was poured into PTFE (polytetra-floroethylene) molds and cured in the oven. Curing details will be given in Section 2.2.2.

(ii) Group II Specimens: In this group, resin was first mechanically mixed again at 35 ºC for 1 hour. Then, rubber particles without further purification were added to the liquid phenolic resin, and this mixture was mixed by the stirrer, with the rate of 120 rpm, at 45 ºC to dissolve the powder rubber particles. In this group, matrix resin is modified with four different rubber amount; 0.5, 1, 2, and 3% by weight. Therefore, mixing period was not constant; it increased from 6 to 9 hours with the rubber concentration. Finally, resin-rubber mixture was poured into PTFE molds and oven cured.

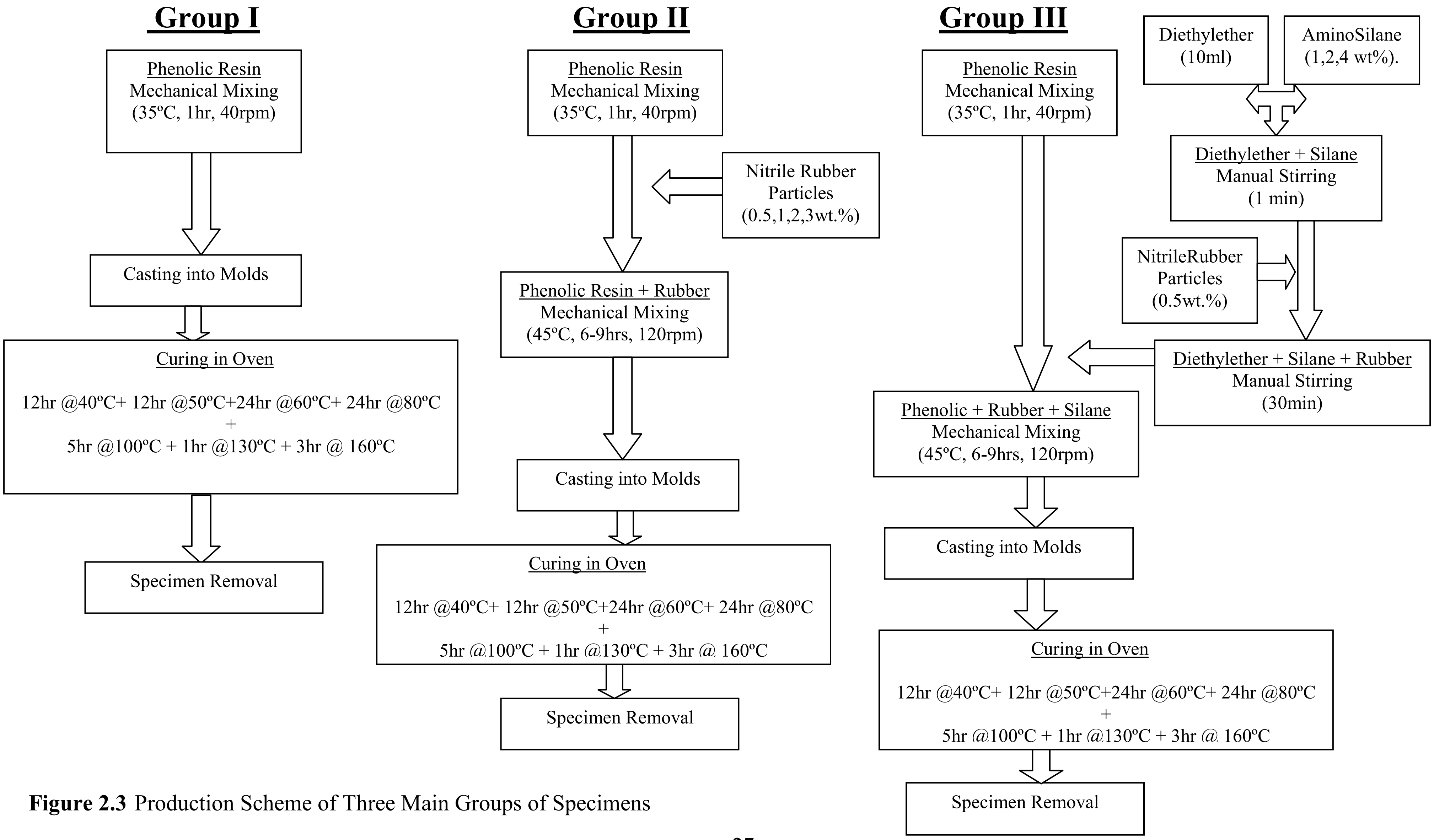


Figure 2.3 Production Scheme of Three Main Groups of Specimens

(iii) Group III Specimens: In this group, first of all, liquid amino silane was dissolved in 10 ml diethylether solvent by stirring manually for 1 minute. Then, nitrile rubber particles were added to this silane-diethylether system. Since, specimens having 0.5 wt % rubber content resulted in highest performance in the previous group, it was decided to use only this rubber content (0.5 wt %) in this group. But, to investigate the effects of amino silane addition, three different silane concentrations were used; 1, 2, and 4 % by weight with respect to the amount of rubber particles.

Solvent-rubber-silane mixture was kept at room temperature for 30 minutes for the evaporation of the solvent. Then, this silane-rubber mixture was added to the mechanically mixed (at 35 ºC for 1 hour) resin system. Next, this resin-rubber-silane mixture was mechanically mixed (120 rpm, 45ºC, 6-9 hrs), and finally poured into the mold to cure.

2.2.2 Curing Schedule

As it is explained previously, phenolic resins should be cured carefully due to the evaporation of the by-product water molecules leading to void formation in the specimens. In this study, various trials were conducted to obtain an efficient curing schedule. First, high curing temperatures like 160ºC was used and it was observed that specimens were cured in only 30 minutes. However, due to the formation of large amount of bubbles, entire structure was useless. Therefore, it was decided to decrease the curing temperature gradually. Even use of 100ºC resulted in some void formations.

After these unsatisfactory trials, curing temperature was decreased to a very low level, 40ºC. In this case, there was no bubble formation, but, curing period was not practical, for instance in one trial it was observed that a period of 4 days was not enough to obtain a rigid crosslinked structure.

Therefore, it was decided to cure the specimens starting from low temperatures with successive increases. Thus, the most suitable curing schedule obtained was as follows: 12 hours at 40ºC and another 12 hours at 50ºC followed by 24 hours at 60ºC and finally another 24 hours at 80ºC. However, this cure scheme was not enough to obtain a specimen with sufficient mechanical properties. Therefore specimens were post-cured at 100ºC for 5 hours and then 130ºC for 1 hour and finally 160ºC for 3 hours. The overall curing schedule used for all groups of specimens is given in Table 2.4.

Table 2.4 Curing Schedule Used for All Groups of Specimens

Curing	12hr@40ºC + 12hr@50ºC +24hr@60ºC + 24hr@80ºC
Post Curing	5hr@100ºC + 1hr@130ºC + 3hr@160ºC

After curing, specimens were removed from the molds and characterized with 8 different designations. These designations are explained in detail in Table 2.5.

Table 2.5 Specimen Designation Used

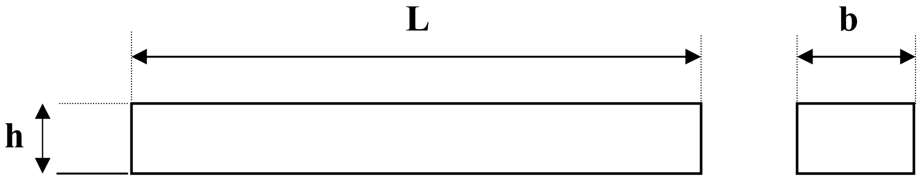
Designation	Specimens
P	Neat phenolic resin
PR0.5	Phenolic resin with 0.5 wt.% nitrile rubber
PR1	Phenolic resin with 1 wt.% nitrile rubber
PR2	Phenolic resin with 2 wt.% nitrile rubber
PR3	Phenolic resin with 3 wt.% nitrile rubber
PRS1	Phenolic resin with 0.5 wt. % nitrile rubber and 1 wt.% amino silane (with respect to nitrile rubber)
PRS2	Phenolic resin with 0.5 wt. % nitrile rubber and 2 wt.% amino silane (with respect to nitrile rubber)
PRS4	Phenolic resin with 0.5 wt. % nitrile rubber and 4 wt.% amino silane (with respect to nitrile rubber)

2.3 Mechanical Tests

Flexural, notched Charpy impact and plane-strain fracture toughness tests were performed in order to characterize the mechanical behaviors especially toughness of the specimens. Tests were carried out at room temperature and at least 5 samples were tested.

2.3.1 Flexural Tests

Flexural properties of the specimens were determined by three point bending tests according to ISO 178 standard. The shape and the dimensions of the specimens are given in Figure 2.4. Tests were carried out by a 10 kN Shimadzu AGS-J universal testing machine with a constant loading rate of 1 mm/min.



L = Specimen length………………… 80 mm

b = Specimen width…………………..10 mm

Figure 2.4 Three-Point Bending Test Specimen

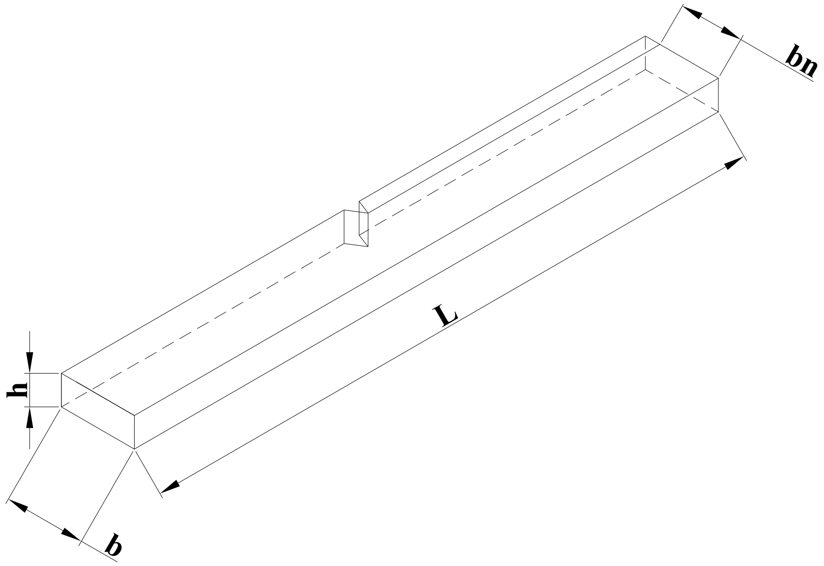
The following relations were used to convert load and deflection data into flexural stress and flexural strain values;

$$\sigma = \frac{3FL}{2bh^2} \quad ; \quad \varepsilon = \frac{6h\delta}{L^2}$$

where *F* is the applied force, *δ* is the deflection, *L*, *b* and *h* are the span length, width and thickness of the specimen, respectively. To calculate flexural modulus (*E*), slope of the linear part of the flexural stress versus flexural strain curve was used. Flexural stress versus flexural strain curves of the specimens are given in Appendix B.

2.3.2 Notched Charpy Impact Tests

Charpy impact tests were performed by using Coesfeld Material Test Unit according to ISO 179-1 standard with Type 1A specimens. The dimensions of these single-edge notched specimens were given in Figure 2.5.



L = Specimen length…………………80 mm
h = Specimen thickness………………4 mm
b = Specimen width…………………..10 mm
b_n = Remaining width…………………8 mm

Figure 2.5 Charpy Single-Edge Notched Specimen

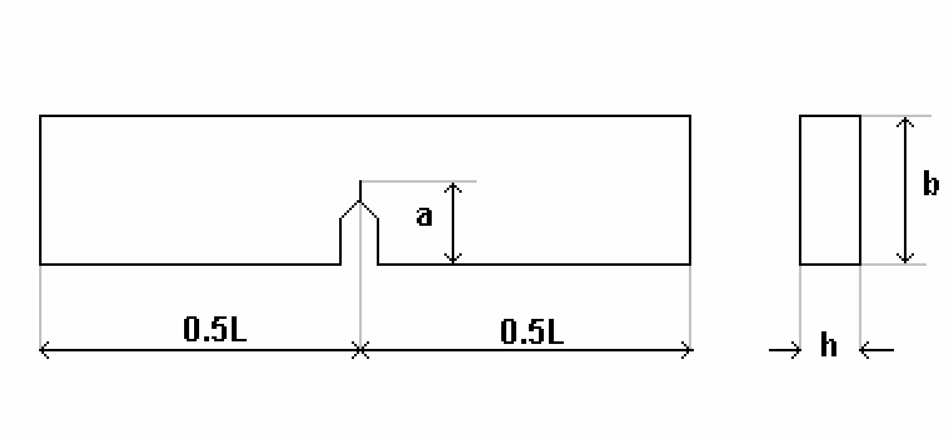
Charpy impact strength of notched specimens, a_{cN}, expressed in kilojoules per square meter, was calculated according to the following equation:

$$a_{cN} = \frac{E_c}{hb_n} \times 1000$$

where E_c is the corrected energy, in joules, absorbed by breaking the test specimen.

2.3.3 Plane-Strain Fracture Toughness Tests

Fracture toughness tests were performed according to ISO 13586 standard with single-edge notched bending (SENB) specimens (Figure 2.6). Specimens were first pre-cracked by a razor and then fractured by a 10 kN Shimadzu AGS-J universal testing machine with a constant loading rate of 10 mm/min.



L = Specimen length…………………80 mm
h = Specimen thickness………………4 mm
b = Specimen width…………………..10 mm
a = Crack length……………………..4.5-5.5 mm

Figure 2.6 Single-Edge Notched Bending (SENB) Specimen

In order to calculate plane-strain fracture toughness value, K_{IC}, the following formula was used;

$$K_Q = f(\alpha) \times \frac{F_Q}{h\sqrt{b}} \quad \text{where} \quad \alpha = a/b \quad (0 < \alpha < 1) \text{ and}$$

$$f(\alpha) = 6\sqrt{\alpha}\ \frac{1{,}99 - \alpha(1-\alpha)(2{,}15 - 3{,}93\alpha + 2{,}7\alpha^2)}{(1+2\alpha)(1-\alpha)^{3/2}}$$

F_Q is the load at crack growth initiation and $f(\alpha)$ is the geometry calibration factor. h and b are the thickness and width of the test specimen respectively.

Load at crack growth initiation, $F_{Q,}$ is determined from load-displacement curve which has a linear behavior with an abrupt drop. In this linear curve, the maximum value of load (F_{max}) corresponds to F_Q. Load versus deflection curves of specimens are given in Appendix C. For the assessment of K_{IC} value, K_Q should satisfy the validity equation so that K_Q is equal to K_{IC}. If not, a thicker and/or more deeply precracked sample should be prepared.

2.4 Fractographic Analysis by SEM

Fracture surfaces obtained from flexural and plane-strain fracture toughness test specimens were examined by using JEOL JSM-6400 type Scanning Electron Microscope. Fractographic studies were especially used to determine possible rubber toughening mechanisms and distribution and interactions of rubber domains with the phenolic matrix. Before SEM examinations, specimen surfaces were cleaned by an ultra-sonic cleaner and coated with a thin layer of gold palladium alloy by sputtering.

2.5 Thermal Analysis by DMA

In dynamic mechanical analysis (DMA), samples are subjected to a periodically varying sinusoidal stress. The response of the material to this treatment can provide information on its viscoelastic properties. Although most classical materials exhibit either an elastic or a viscous response to an applied load, polymers because of their viscoelasticity give a response somewhere between these two extremes (pure elastic and pure viscous). Their response in terms of modulus can be characterized by the “elastic” or “storage” modulus (E’) and the “viscous” or “loss” modulus (E’’) [43]. The ratio between the loss modulus (out-of-phase component) and the storage modulus (in-phase component) is the tangent of the phase angle, δ. By the establishing of *Tanδ* which is also known as loss tangent versus temperature curve, it can be possible to identify the onset of specific types of molecular motions like glass transition temperature.

Perkin-Elmer Diamond type dynamic mechanical analyzer was used in order to obtain especially storage modulus (*E'*) and glass transition temperature (T_g) data. Thermal analysis of the bar specimens 60 x 10 x 4 mm under bending mode were carried out for a temperature range of 25 to 250 ºC with a constant heating rate of 10 ºC/min and at a constant frequency of 1 Hz. DMA curves of the specimens are given in Appendix D.

CHAPTER III

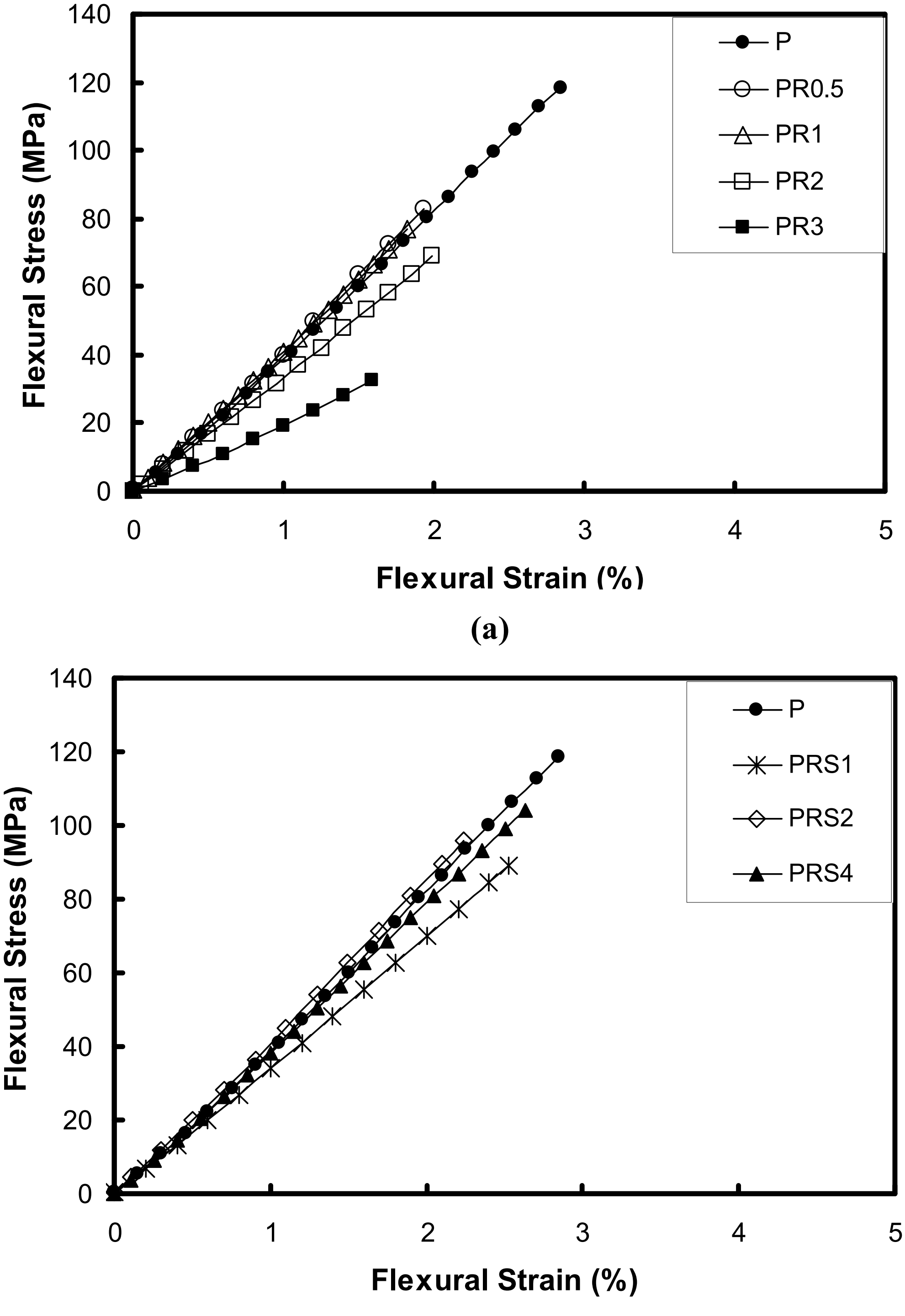
RESULTS AND DISCUSSION

3.1 Mechanical Test Results

In this study, mechanical properties especially toughness of the resol type phenolic resin modified by nitrile rubber particles and an amino silane were examined experimentally. For this purpose, flexural, notched charpy impact and plane-strain fracture toughness tests were performed and, flexural strength, flexural strain break, flexural modulus, impact strength and fracture toughness values were obtained accordingly. For each test at least 5 specimens were tested.

3.1.1 Flexural Tests

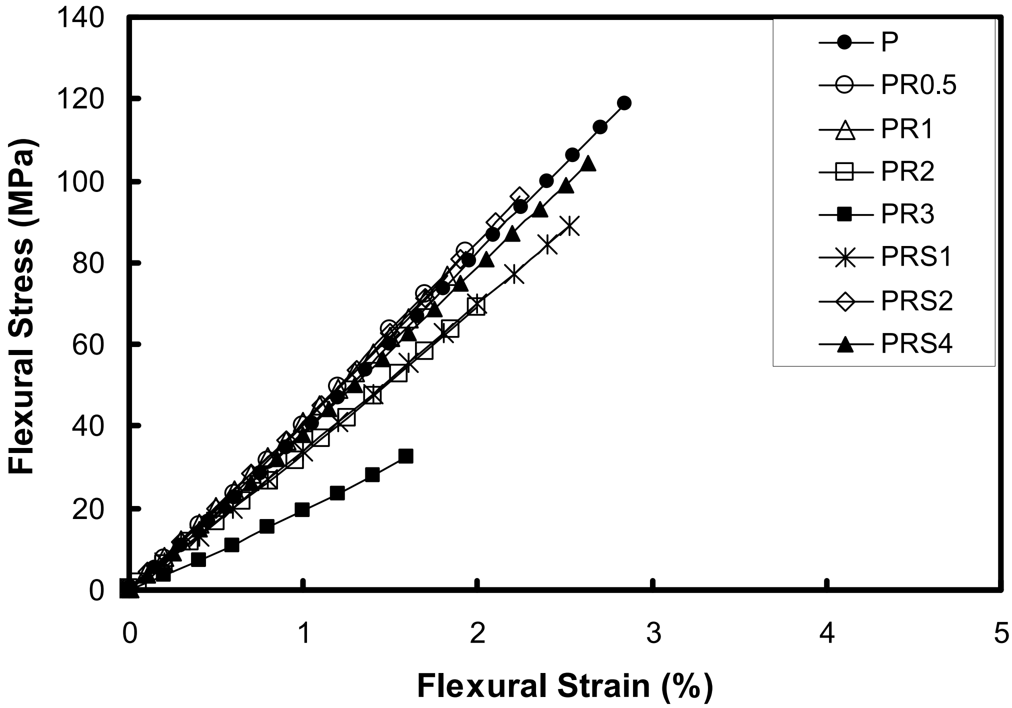
After performing these tests, data were first evaluated as “flexural stress” versus “flexural strain” curves. These curves for each specimen are given in Appendix B. Then, in order to compare flexural behavior of all groups, these curves are evaluated on the same chart (Fig. 3.1), first for only rubber modified specimens (Fig. 3.1(a)), secondly for rubber and silane modified specimens (Fig. 3.1(b)), and also for all specimens together (Fig. 3.1(c)). Note that neat phenolic resin specimen (P) is also included in each chart.



(a)

(b)

Figure 3.1 Flexural stress versus flexural strain curves for; (a) only rubber modified specimens, (b) rubber and silane modified specimens, and (c) all specimens



(c)

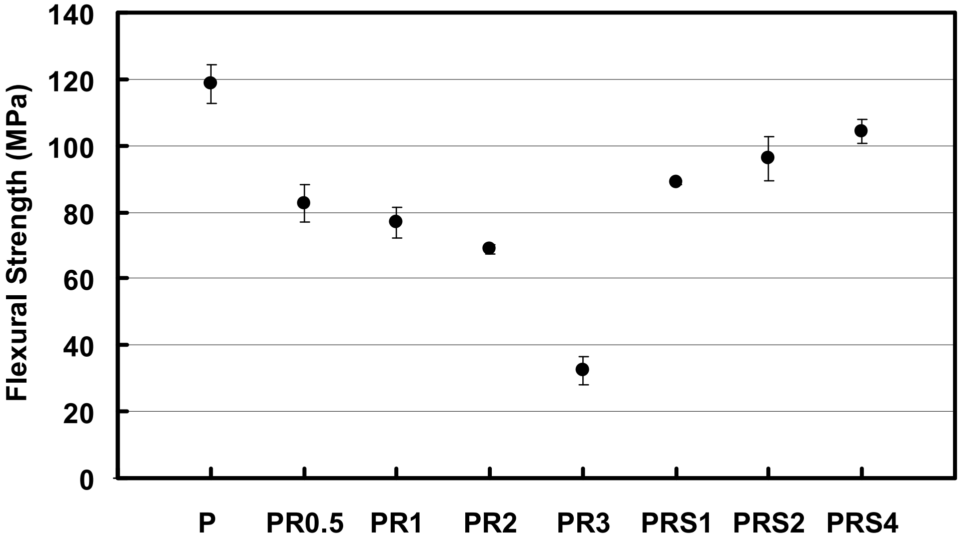
Figure 3.1 (continued)

Finally, these curves are used to determine flexural strength, flexural strain at break and flexural modulus values of all specimens. These mechanical properties are first tabulated in Table 3.1 and then compared for each specimen in Figure 3.2.

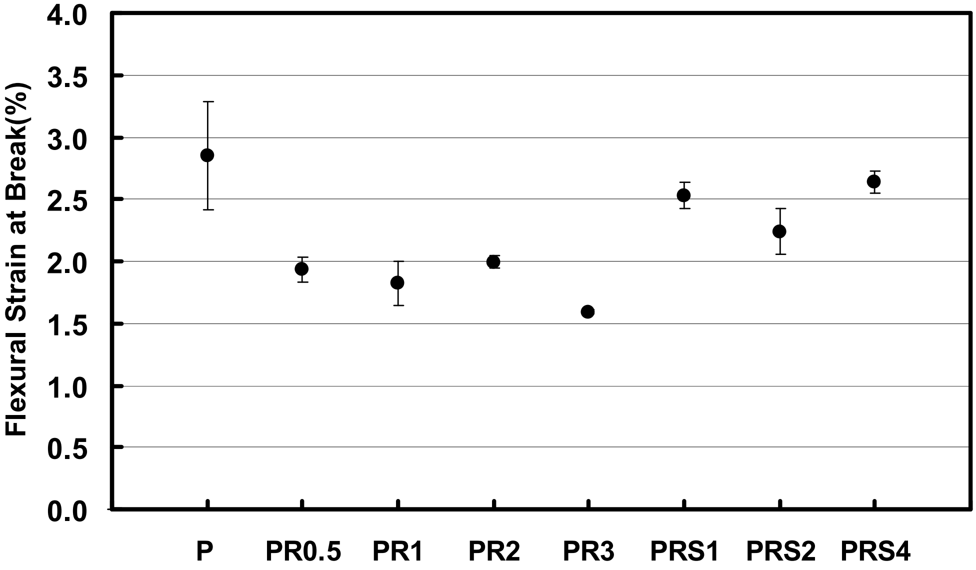
Table 3.1 Flexural Test Results of all specimens

Specimen Designation*	Flexural Strength (MPa)	Flexural Strain at Break (%)	Flexural Modulus (GPa)
P	119 ± 6	2.85 ± 0.44	3.58 ± 0.10
PR0.5	83 ± 6	1.93 ± 0.10	3.82 ± 0.05
PR1	77 ± 5	1.82 ± 0.18	3.81 ± 0.07
PR2	69 ± 1	1.99 ± 0.05	3.39 ± 0.05
PR3	32 ± 4	1.59 ± 0.02	2.00 ± 0.04
PRS1	89 ± 1	2.53 ± 0.11	3.43 ± 0.04
PRS2	96 ± 7	2.24 ± 0.18	3.67 ± 0.03
PRS4	104 ± 4	2.64 ± 0.09	4.04 ± 0.09

*For details of specimen designation please see Table 2.5

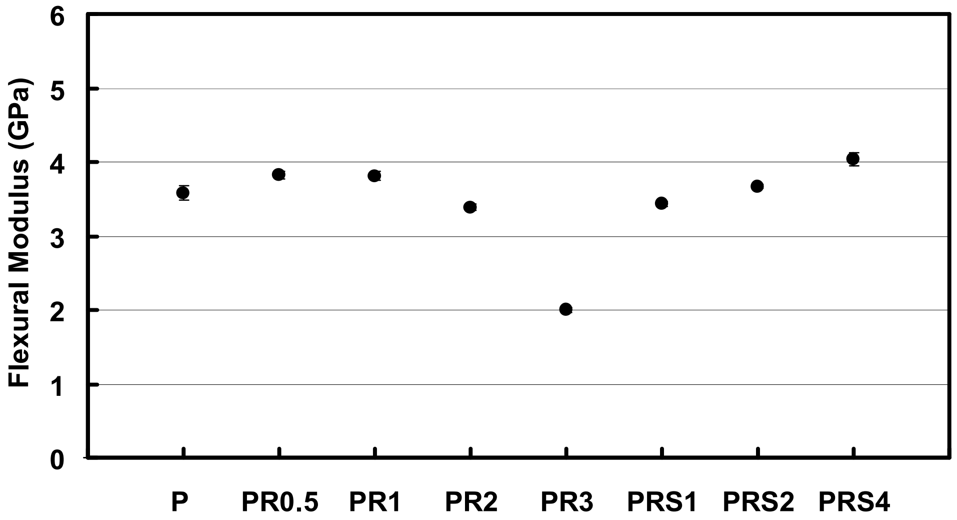


(a)



(b)

Figure 3.2 Flexural properties of all specimens; (a) Flexural Strength, (b) Flexural Strain at Break, and (c) Flexural Modulus



(c)

Figure 3.2 (continued)

Figure 3.2 (a) shows that use of nitrile rubber particles in phenolic matrix decreases flexural strength values of the specimens. These decreases should be due to two main reasons; first of all since nitrile rubbers have elastomeric behavior having low strength, it is reasonable to decrease the flexural strength values of the phenolic matrix. The second reason was the difficulties encountered during specimen production. For instance formation of voids in the specimens due to the water evaporation during very long curing schedules. Another problem in specimen production was the difficulty in dissolving solid rubber particles in liquid phenolic resin, which increased more with increased rubber content.

Figure 3.2 (a) also shows that use of amino silane together with nitrile rubber in the phenolic matrix increases the flexural strength values. For example, specimens having 0.5% rubber and 2% silane (PRS2) and 4%

silane (PRS4) have 16% and 25% higher flexural strength than the specimen having only 0.5% rubber (PR0.5). That can be considered as the “synergistic” effect of amino silane when used together with nitrile rubber particles.

As seen in Figure 3.2 (b), flexural strain at break values also decreases when nitrile rubber particles are used in the phenolic matrix. Normally, since these particles are elastomeric materials, strain values should increase. Unfortunately, due to the specimen production problems discussed above, this was not observed. Void formation and debonded solid rubber particles led to lower strain values at failure. However, synergistic effect of amino silane with nitrile rubber increased these strain values. For instance, strain at failure values increased 16% and 37% in the specimens PRS1 and PRS4 respectively compared to PR0.5 specimen.

Figure 3.2 (c) indicates that flexural modulus values do not decrease when phenolic matrix was modified with nitrile rubber particles, except for the specimen PR3 having the highest rubber content, which should be again due to the specimen production problems mentioned above. Use of amino silane with nitrile rubber increased the modulus values slightly, the highest increase being 13% in the specimen PRS4 compared to neat phenolic specimen P.

3.1.2 Charpy Impact Tests

Charpy impact strength values were first tabulated in Table 3.2 together with plane-strain fracture toughness values, and then compared for all specimens in Figure 3.3.

Table 3.2 Charpy Impact and Plane-Strain Fracture Toughness Test Results of all specimens

Specimen Designation*	**Charpy Impact Strength (kJ / m^2)**	**Fracture Toughness (MPa√m)**
P	1.17 ± 0.08	1.02 ± 0.13
PR0.5	1.82 ± 0.12	1.22 ± 0.06
PR1	1.60 ± 0.11	1.15 ± 0.03
PR2	1.22 ± 0.20	1.10 ± 0.07
PR3	0.89 ± 0.05	0.83 ± 0.15
PRS1	1.70 ± 0.17	1.41 ± 0.02
PRS2	1.90 ± 0.18	1.53 ± 0.07
PRS4	1.24 ± 0.06	1.39 ± 0.08

* For details of specimen designation please see Table 2.5

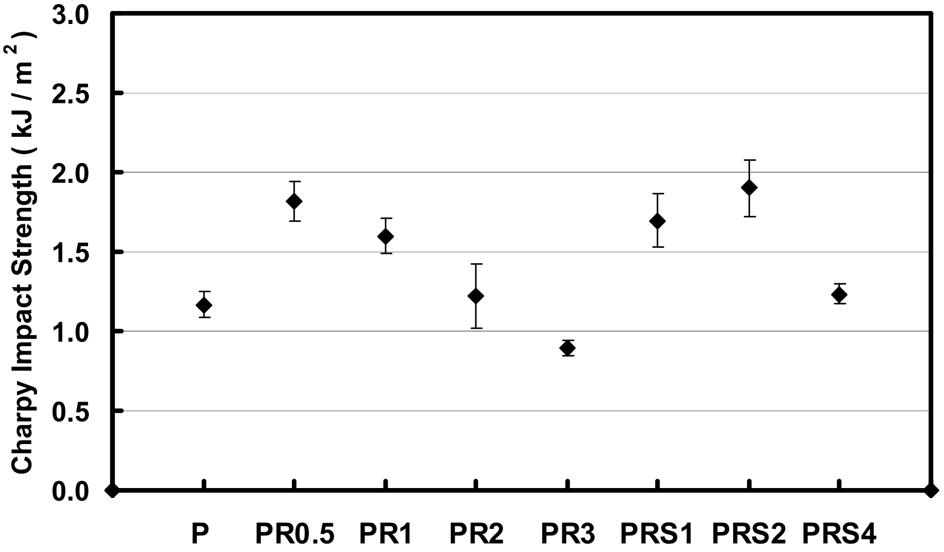


Figure 3.3 Charpy Impact Strength values of all specimens

Figure 3.3 shows that Charpy impact strength value of neat phenolic specimen (P) was improved when modified with nitrile rubber particles, the increases for instance being 56% and 37% in the specimens PR0.5 and PR1 respectively. This is reasonable due to the "rubber toughening" effect of nitrile rubber domains in the phenolic matrix.

However, increasing rubber content decreases the improvement so that the specimen having highest rubber content (PR3) had lower impact strength than the neat phenolic specimen (P). This should be again due to the problems during specimen production. As the rubber content increases, time period required to dissolve these rubber particles in liquid phenolic resin also increases. These longer periods lead to some precuring in the phenolic structure and make the mixture more viscous. Due to the difficulty in stirring the more viscous mixture, very small air bubbles were introduced into the mixture. Although many of these bubbles leave the system from the surface, some of them especially located at the bottom can not escape. As a result, these tiny voids at the bottom surface make the specimen more brittle by acting as stress risers or cracks.

Figure 3.3 also shows that use of amino silane together with nitrile rubber increases Charpy impact strength value of the neat phenolic specimen (P) significantly. This synergistic increase in rubber toughening was as much as 46% and 63% in the specimens PRS1 and PRS2 respectively.

3.1.3 Plane-Strain Fracture Toughness Tests

After performing these tests, data were first evaluated as “load” versus “deflection” curves. These curves for each specimen are given in Appendix C. Then, by using these curves and the rules and relations given in Section 2.3.3, plane-strain fracture toughness values were determined. These fracture toughness values are tabulated in Table 3.2, and for comparison given in Figure 3.4.

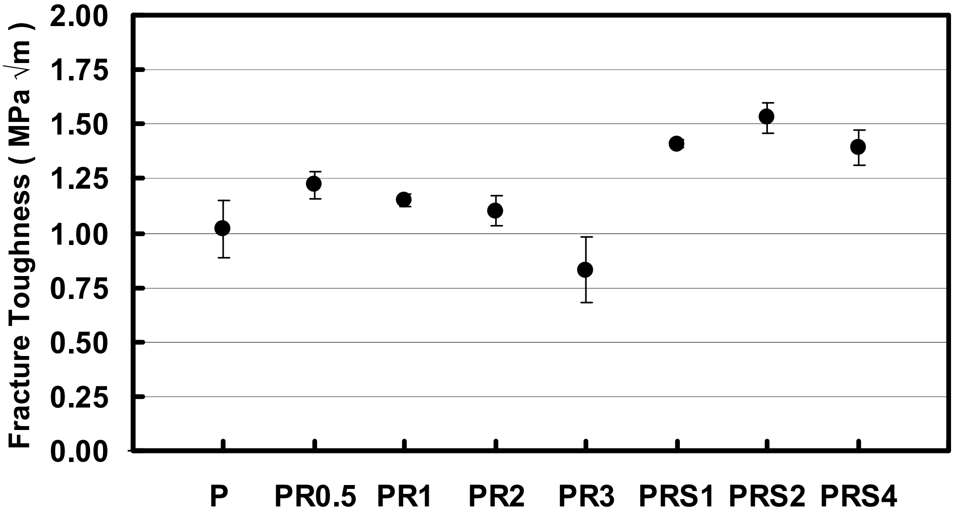


Figure 3.4 Plane-Strain Fracture Toughness values of all specimens.

Figure 3.4 indicates that fracture toughness test results are very well correlated with the Charpy impact test results. That is, when the neat phenolic specimen (P) is modified with nitrile rubber, its fracture toughness increases 20%, 13%, and 8% in the specimens PR0.5, PR1, and PR2, respectively. Again, increasing rubber content decreases the improvement due to the specimen production difficulties discussed before.

Figure 3.4 also indicates that rubber toughening is more effective when nitrile rubber was used together with amino silane. In this synergistic case, fracture toughness of the neat phenolic specimen (P) increases 38%, 50% and 36% in the specimens PRS1, PRS2, and PRS4, respectively.

Toughness improvement via rubber toughening was achieved by the formation of rubber domains and silane domains which delay and/or decrease the growth rate of main and secondary cracks propagating in the stiff but brittle phenolic matrix.

Thus, phenolic resin gains some toughening by several energy absorption mechanisms as explained previously. Some of these mechanisms could be rubber stretching, multilevel fracture path, crack deflection, crack pinning, and the shear deformation which is the main toughening mechanism for thermosets.

3.2 Fractographic Analysis by SEM

Fracture surfaces of many fracture toughness and flexural test specimens were analyzed by using scanning electron microscope (SEM), especially to observe rubber toughening mechanisms.

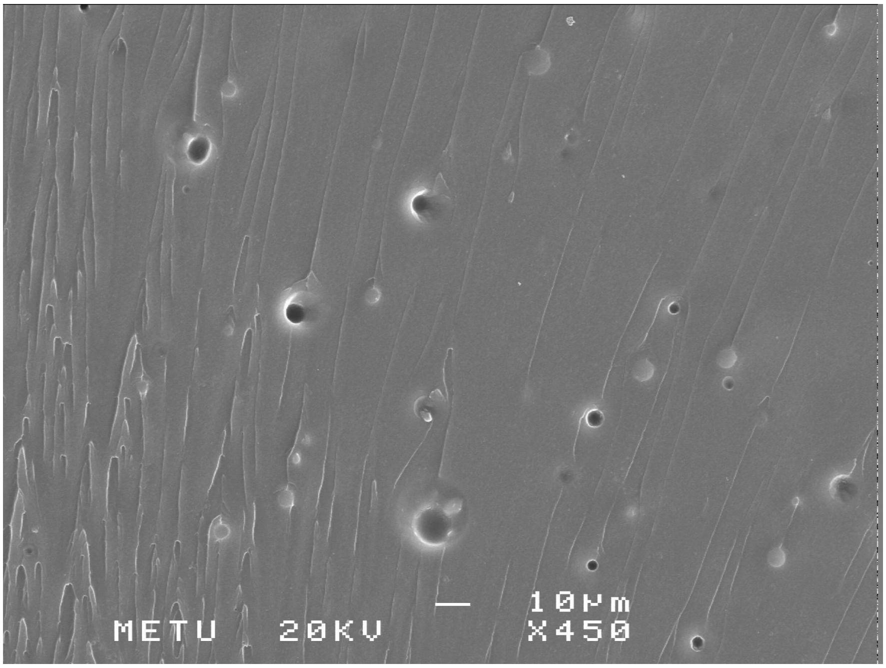
Low magnification fractographs in Figure 3.5 show that nitrile rubber domains formed in the phenolic matrix are generally uniformly distributed. They also show that increasing the rubber content increases not only the number of the rubber domains, but also amount of deformation lines and the level of fracture surface roughness.

Higher magnification in Figure 3.6 indicates that these nitrile rubber domains have round shapes with a diameter around 10 μm. Closer views in Figure 3.7 also indicate that there is a proper interface between the rubber domains and the phenolic matrix.

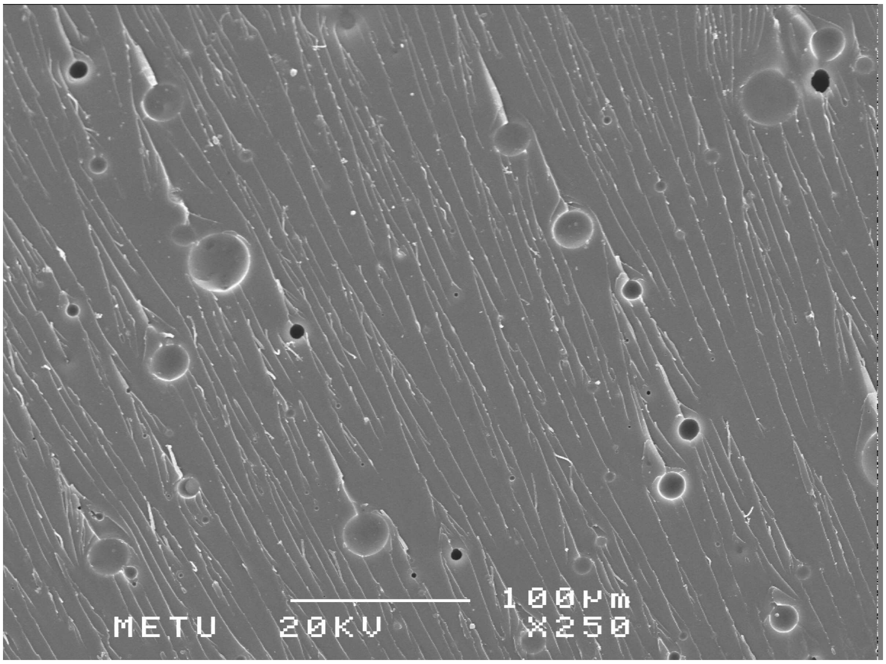
Due to the high viscosity and stirring difficulties mentioned before, when the rubber content was high (e.g. PR3 specimen) not all the rubber particles were dissolved in the liquid phenolic matrix. In this case, some rubber particles remained as solid particles in the crosslinked phenolic structure. Two examples are shown in Figure 3.8. Since rubber particles are not as effective as rubber domains, PR3 specimens had lower mechanical properties.

Figure 3.9 shows that domains of amino silanes formed in the phenolic matrix are similar to the nitrile rubber domains, but they are more spherical and have a lighter color. To differentiate amino silane domains from the nitrile rubber domains, EDX analysis was also carried out. Their diameters are again around 10 μm, and they have also proper interface. Fractographs in Figure 3.10 indicate domains of both nitrile rubber and amino silane together, which resulted in synergistic improvement in rubber toughening of the brittle phenolic structure.

All these fractographs indicated that the main rubber toughening mechanism was shear yielding observed as deformation lines especially initiated at the domains of nitrile rubber and amino silane.

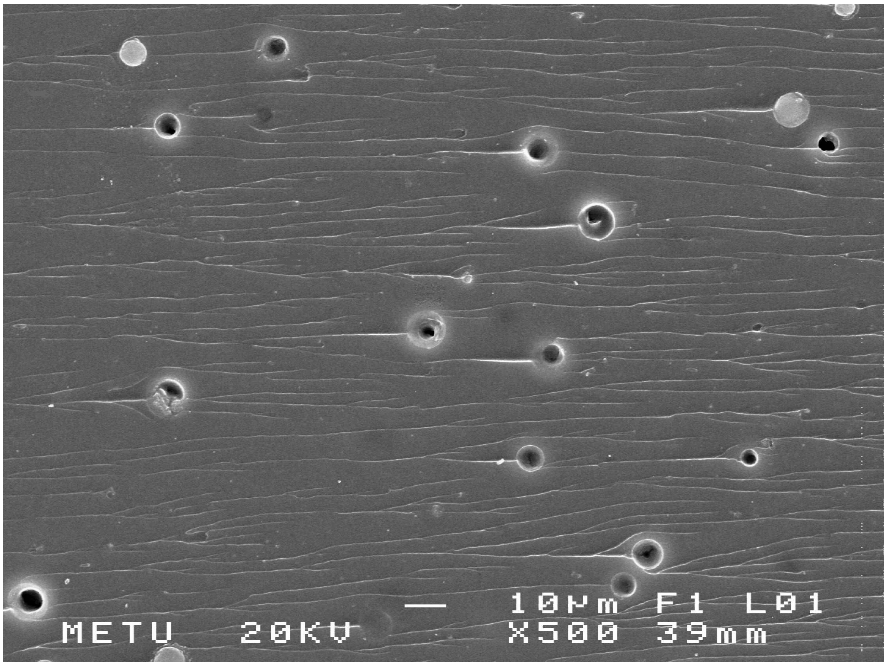


(a)

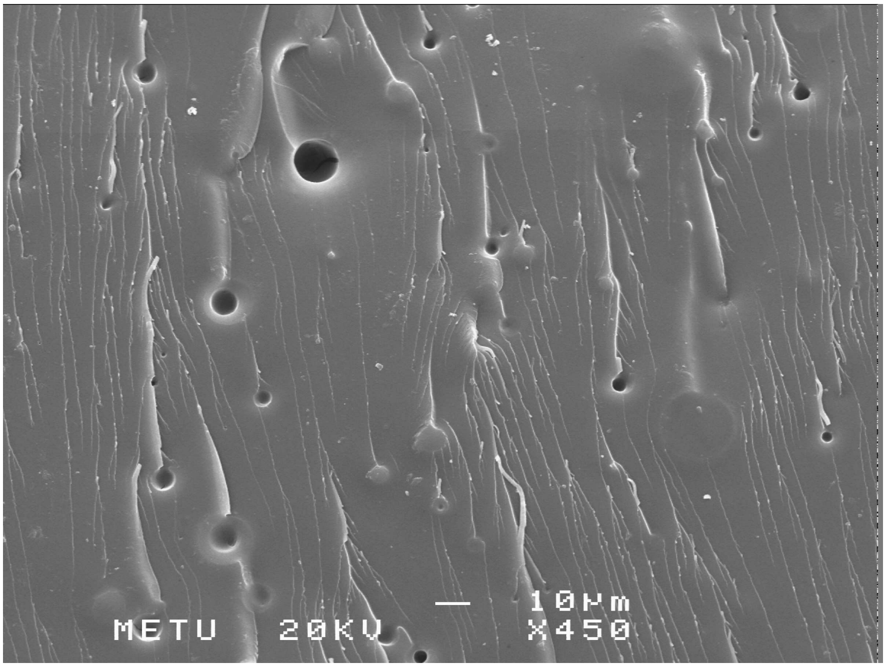


(b)

Figure 3.5 Low magnification fractographs of the specimens; (a) PR0.5, (b) PR1, (c) PR2, and (d) PR3

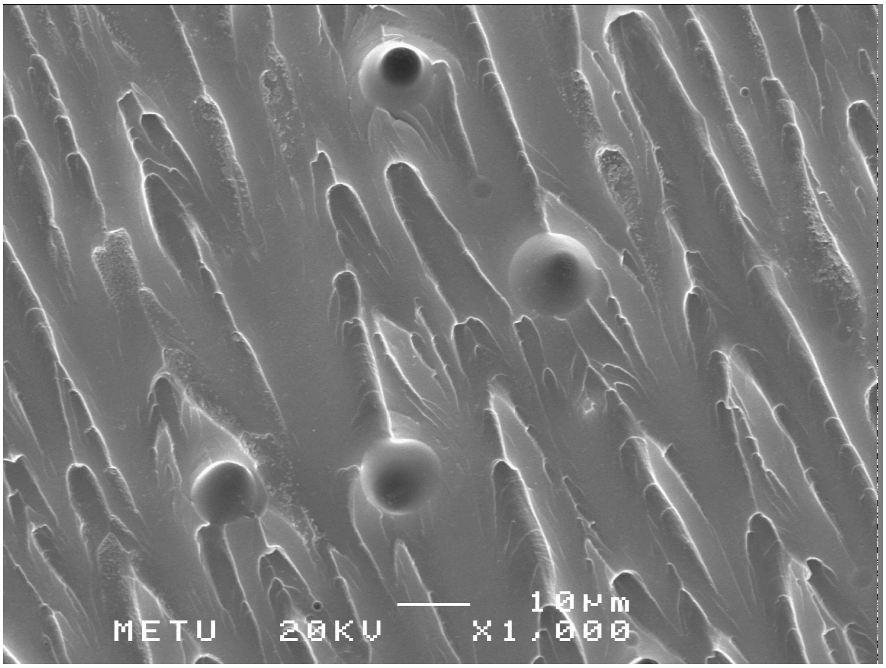


(c)

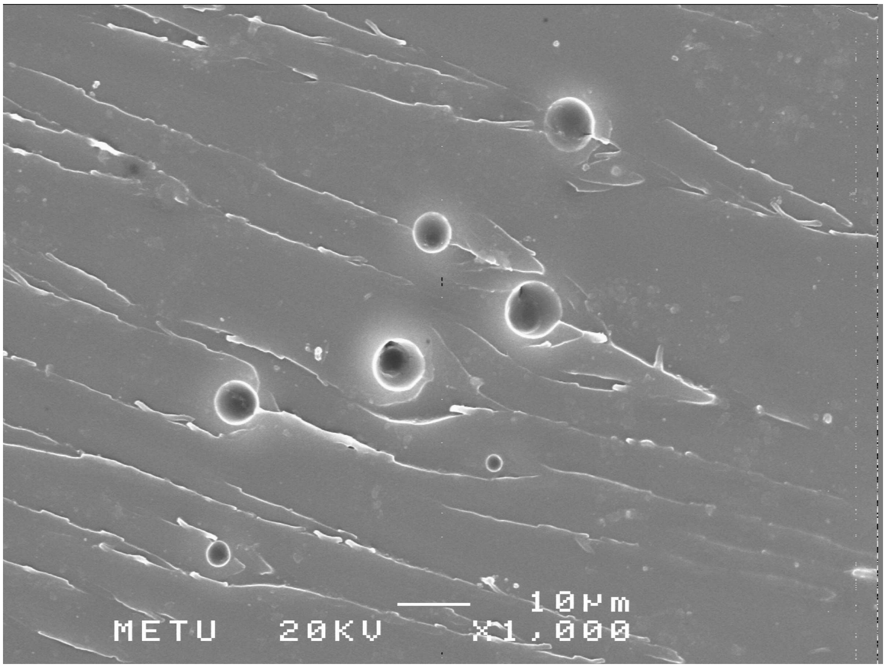


(d)

Figure 3.5 (continued)

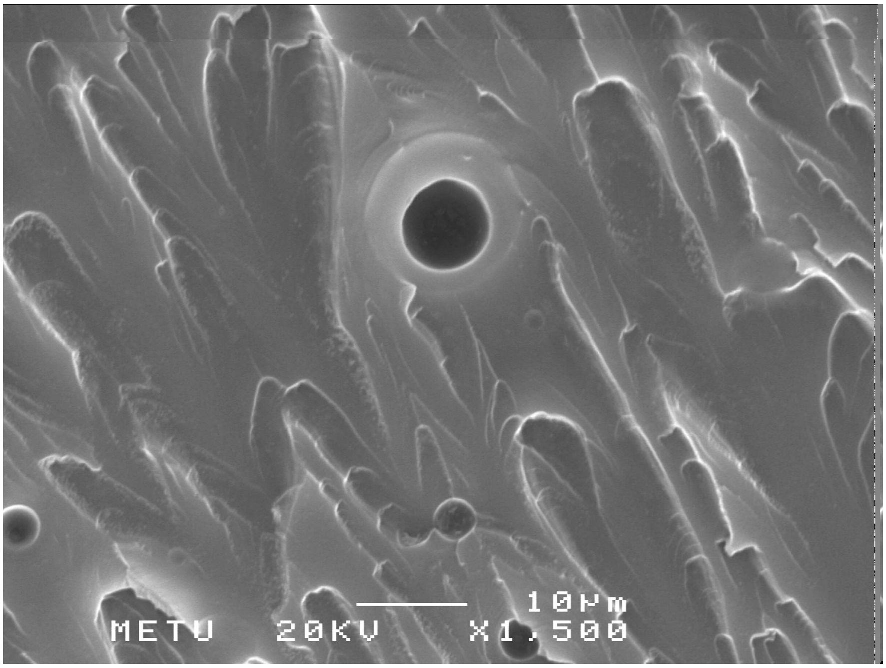


(a)

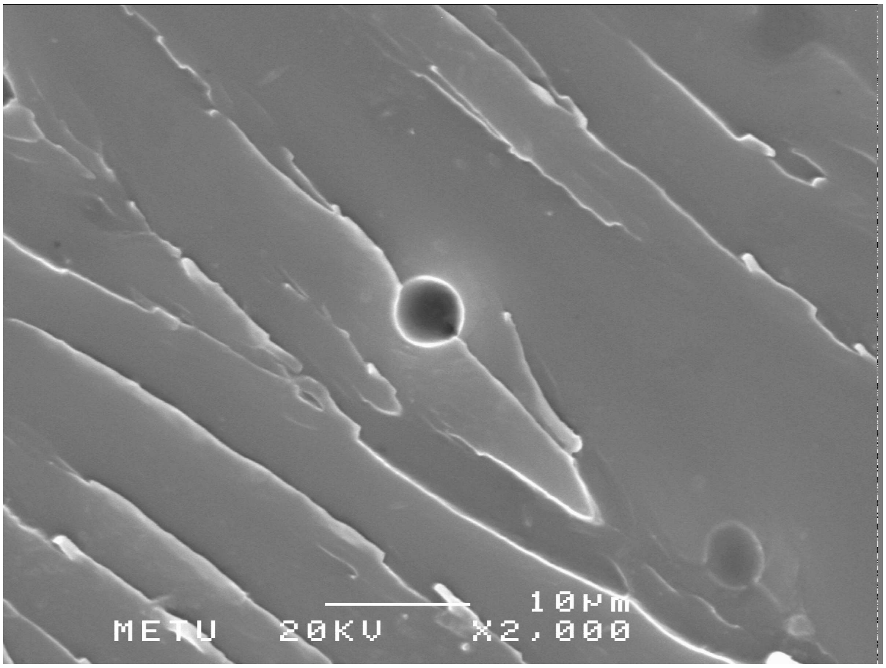


(b)

Figure 3.6 (a), (b), (c), and (d) Four Different High Magnification Fractographs of the PR1 specimen showing Nitrile Rubber Domains and Deformation Lines.

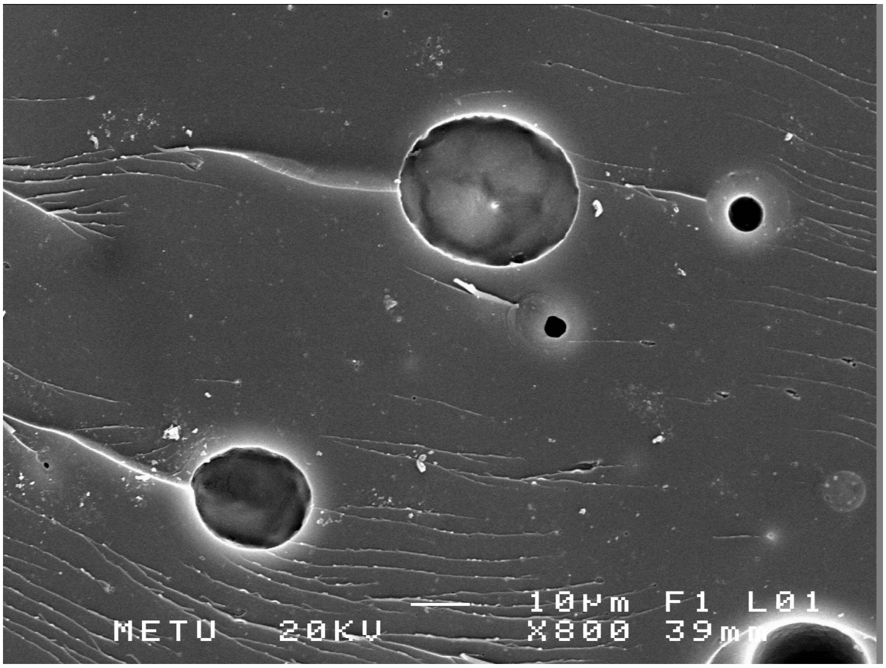


(c)

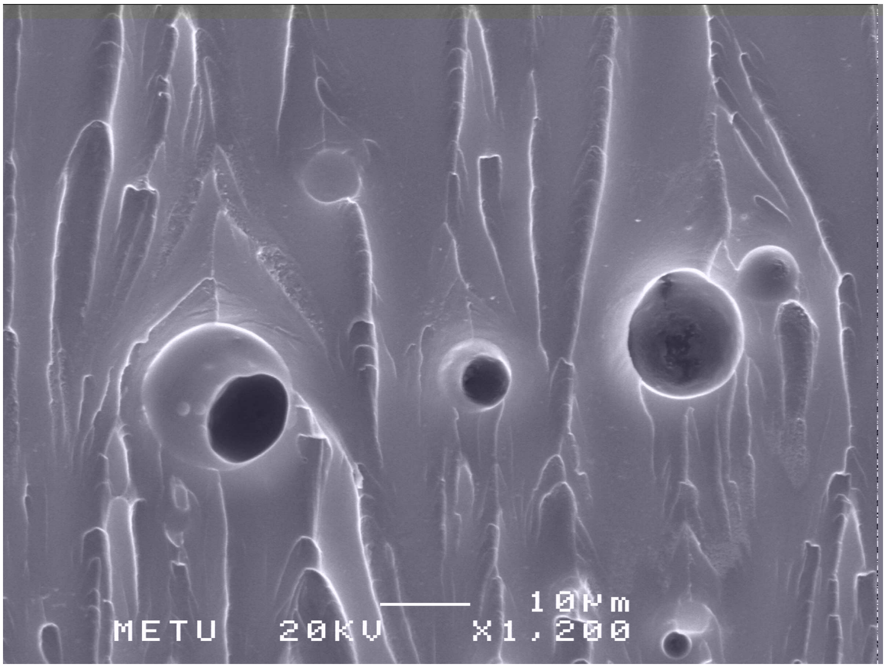


(d)

Figure 3.6 (continued)

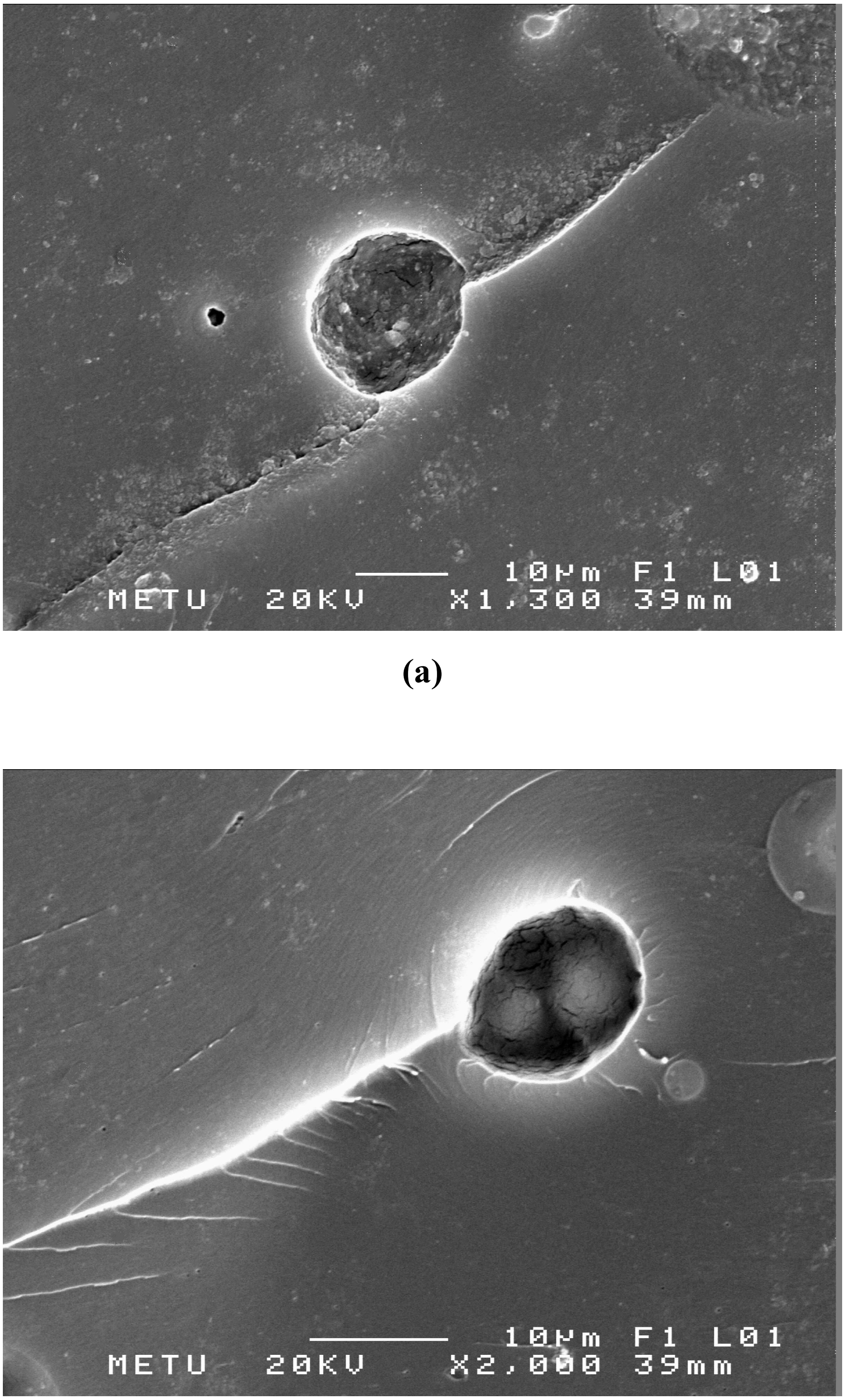


(a)



(b)

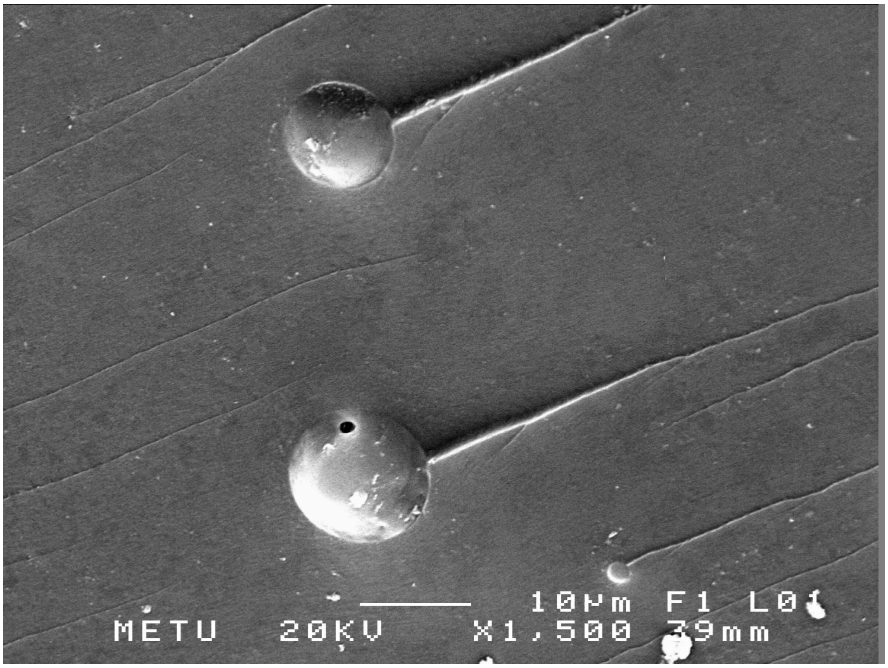
Figure 3.7 (a) and (b) Nitrile Rubber Domains and Deformation Lines in PR1 specimen



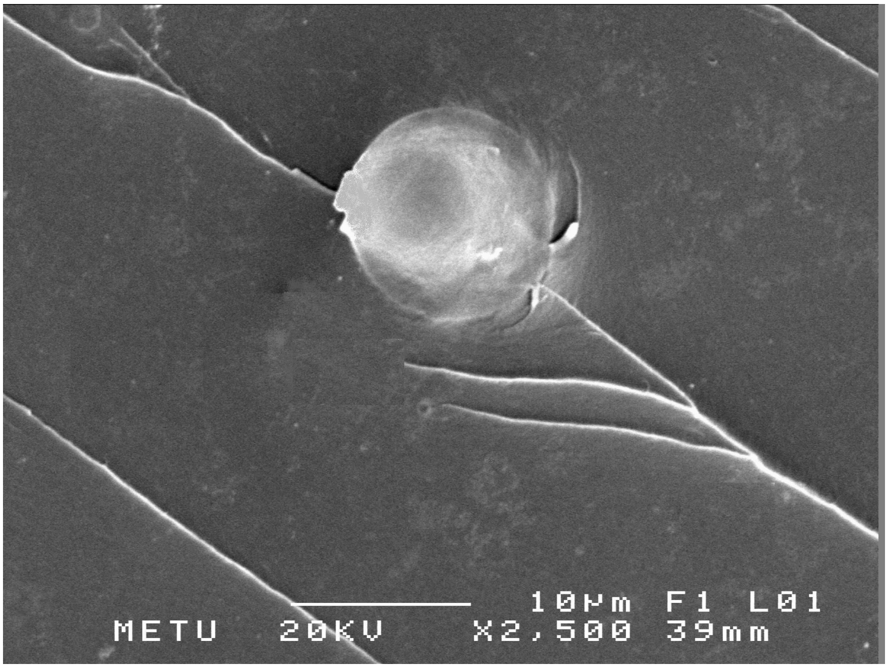
(a)

(b)

Figure 3.8 (a) and (b) Nitrile Rubber Particles and Deformation Lines in PR3 specimen

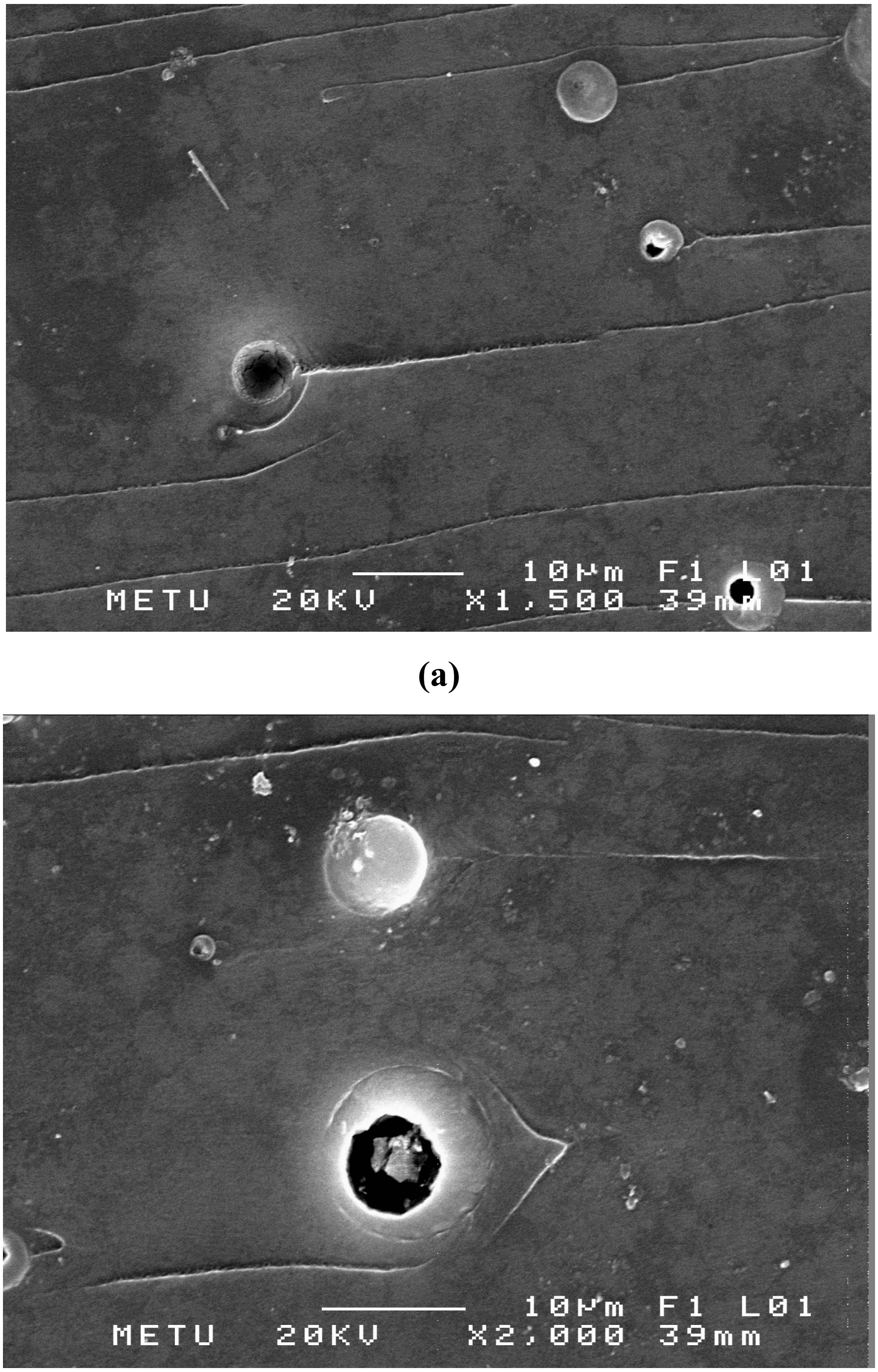


(a)



(b)

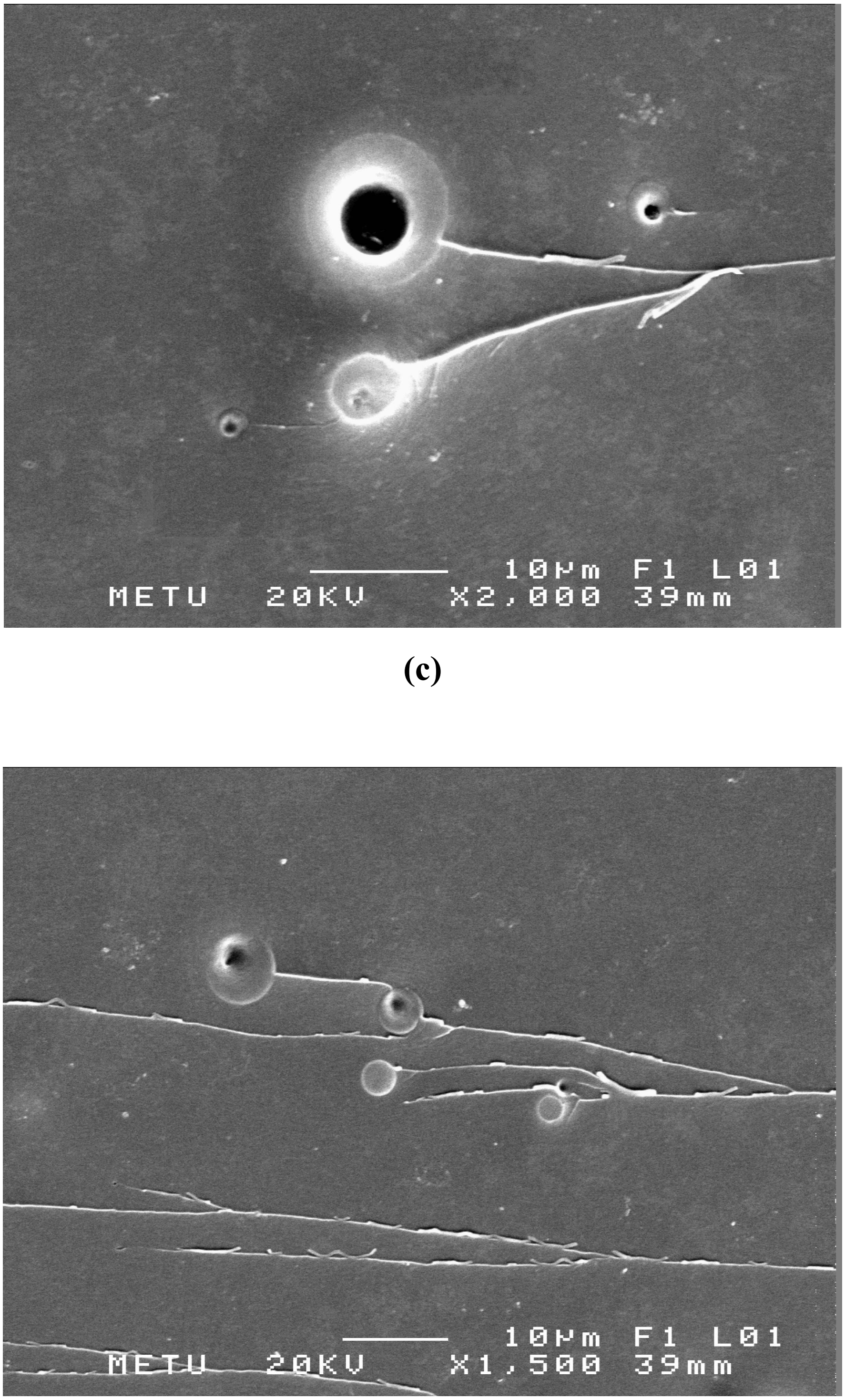
Figure 3.9 Amino Silane Domains and Deformation Lines in (a) PRS1 and (b) PRS4 specimens



(a)

(b)

Figure 3.10 Domains of both Nitrile Rubber and Amino Silane and Deformation Lines in the specimens of; (a) and (b) PRS1, (c) and (d) PRS4



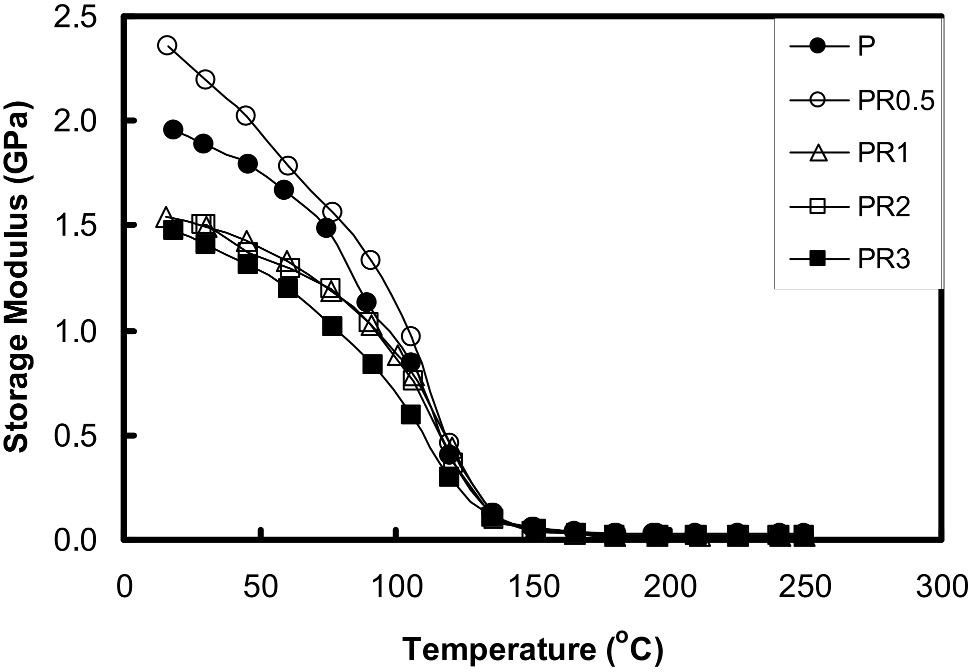
(c)

(d)

Figure 3.10 (continued)

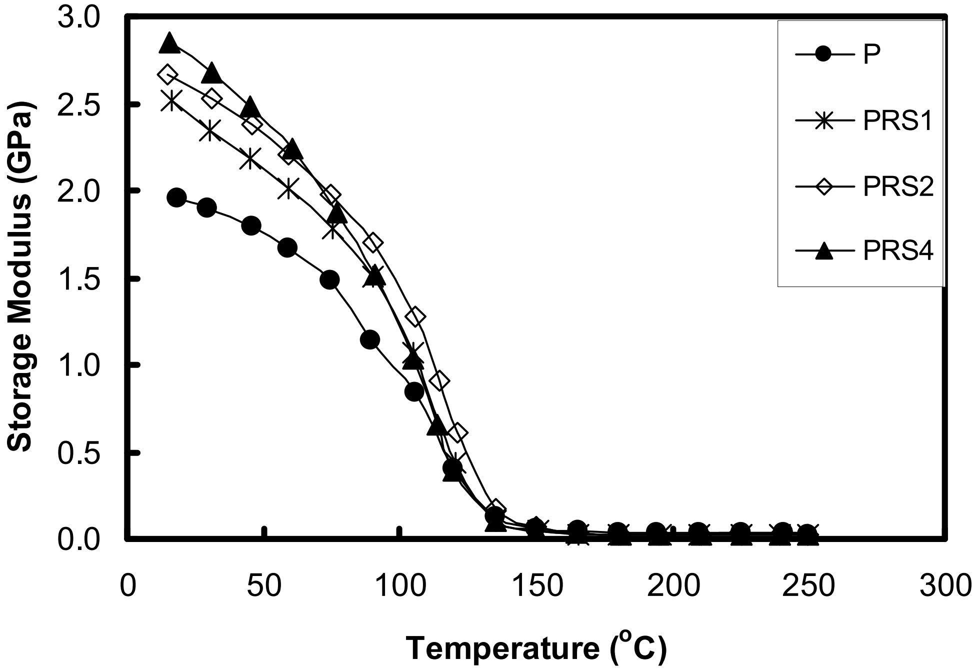
3.3 Thermal Analysis by DMA

In Dynamic Mechanical Analysis, first of all curves of flexural storage modulus (*E'*), flexural loss modulus (*E''*) and loss tangent (*Tanδ*) for each specimen were obtained. They are given in Appendix D. Then, in order to compare thermomechanical properties of all groups; storage modulus versus temperature curves are evaluated on the same chart (Fig. 3.11), first for only rubber modified specimens (Fig. 3.11(a)), secondly for rubber and silane modified specimens (Fig. 3.11 (b)), and also for all specimens together (Fig.3.11 (c)). Note that, neat phenolic resin specimen (P) is also included in each chart.

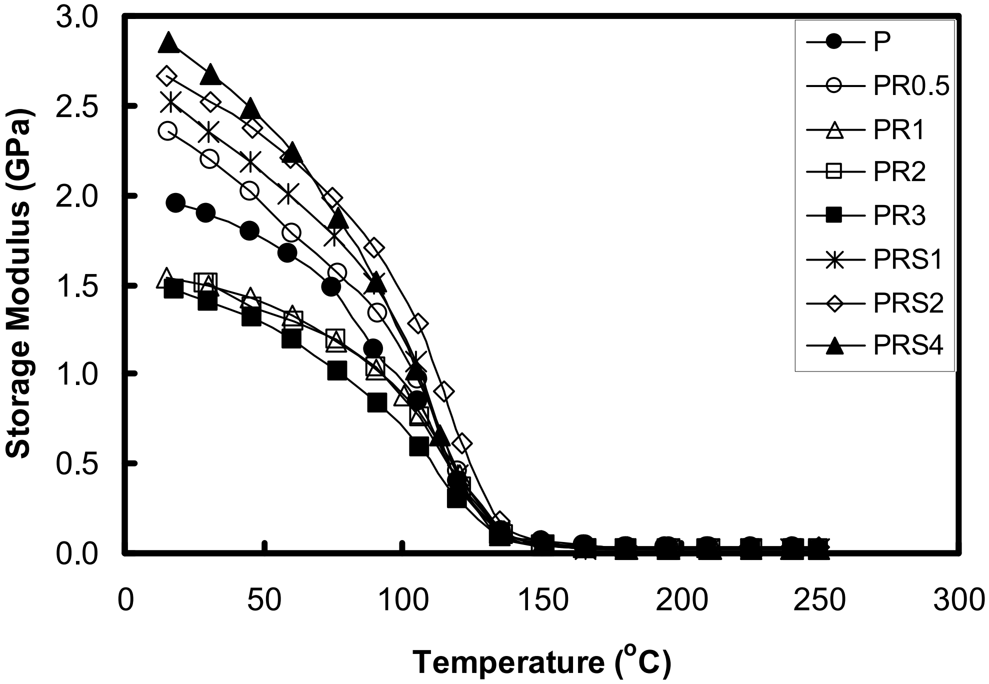


(a)

Figure 3.11 Storage Modulus versus Temperature curves for; (a) only Rubber modified specimens, (b) Rubber and Silane modified specimens, and (c) all specimens



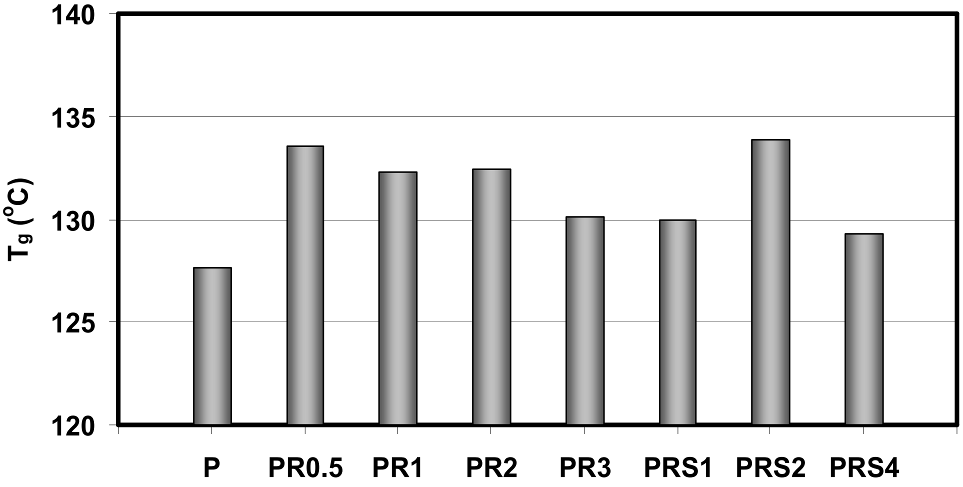
(b)



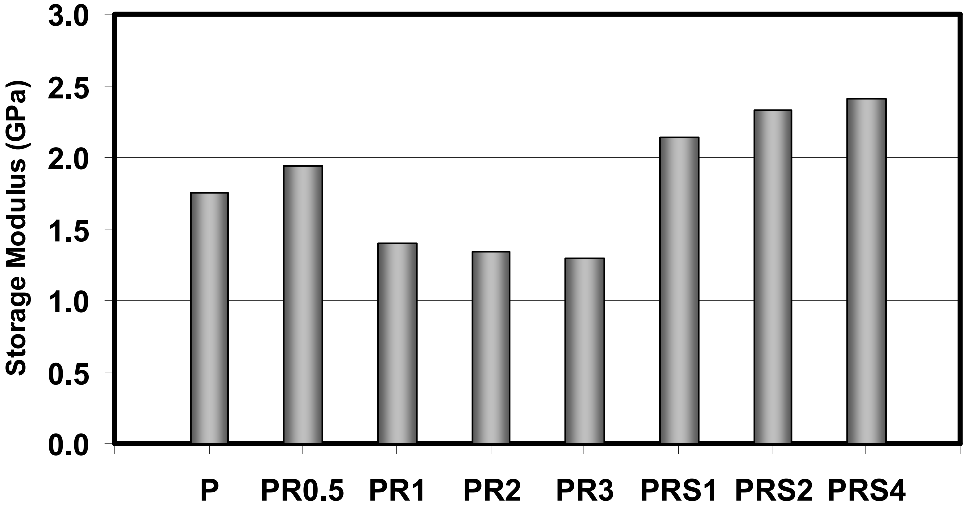
(c)

Figure 3.11 (continued)

Finally, these curves are used to determine the glass transition temperature (T_g) values (peaks of *Tanδ* curves) and storage modulus values (at 50ºC) of all samples. These thermal properties are compared for each specimen in Figure 3.12.



(a)



(b)

Figure 3.12 Thermal Properties of all Specimens; (a) Glass Transition Temperature (*Tanδ* peaks), and (b) Storage Modulus (at 50ºC)

Figure 3.12 (a) shows that T_g of neat phenolic specimen (P) increases slightly when modified by nitrile rubber particles alone or together with amino silane. The highest improvement observed was around 5% in the specimens PR0.5 and PRS2. This might be due to certain interactions between the phenolic matrix and domains of nitrile rubber and amino silane.

As shown in Figure 3.12 (b), storage modulus values (at 50ºC) of neat phenolic specimen (P) increases slightly when modified with very low amount of nitrile rubber (PR0.5). Higher rubber contents decrease the modulus value, possibly due to the specimen production difficulties discussed before. However, when the neat phenolic specimen was modified with nitrile rubber and amino silane together, significant increases in the storage modulus values were obtained, for example 22%, 32%, and 37% in the specimens PRS1, PRS2, and PRS4 respectively. This synergistic effect was also observed in flexural modulus values and other mechanical properties of the samples.

IV

CONCLUSIONS

Specimen preparation by mixing and casting was very difficult. Because;

1. During curing of liquid resol type phenolic resin, release of water molecules (as by product) led to formation of microvoids.

2. In order to minimize void formation, curing temperatures were kept below 100°C, which resulted in extremely long curing times.

3. Use of high nitrile rubber content was not possible, due to the increased viscosity of the mixture and difficulty in stirring leading to undissolved nitrile rubber particles.

From the results of mechanical and thermal tests and fractographic analysis following conclusions are drawn:

1. Flexural strength of the neat phenolic resin specimen decreased when modified with nitrile rubber due to both its elastomeric nature and the specimen production difficulties mentioned above. However, use of amino silane together with nitrile rubber increased the flexural strength value as much as 25% compared to the specimens modified by only nitrile rubber.

2. Charpy impact strength of the neat phenolic resin specimen increased (as much as 56%) when modified with only nitrile rubber. Use of amino silane together with nitrile rubber was more effective leading to increases up to 63%.

3. Similarly, fracture toughness of the neat phenolic resin specimen increased up to 20% when modified with only nitrile rubber, and as much as 50% when modified with nitrile rubber and amino silane together.

4. SEM fractographs indicated that spherical domains on nitrile rubber and amino silanes formed in the phenolic matrix were uniformly distributed, and main rubber toughening mechanism was shear yielding observed as deformation lines especially initiated at these domains.

5. DMA analysis indicated that, glass transition temperature (Tanδ peaks) and storage modulus (at 50°C) of neat phenolic specimen increases slightly when modified by only nitrile rubber or together with amino silane.

It can be finally concluded that rubber toughening of liquid resol type phenol-formaldehyde resin was possible when modified by acrylonitrile rubber. These was a synergistic effect if nitrile rubber was used together with 3-aminopropyltriethoxysilane. The best modifier combination leading to highest properties was 0.5 wt.% nitrile rubber and 2 wt.% amino silane (with respect to nitrile rubber)

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APPENDIX A

Table A.1 General properties of Phenol-Formaldehyde Resins [2]

Classification	**One-Step (Resol)**		**Two-Step (Novolac)**
	A	**B**	
Reaction Catalyst	Strong Bases, i.e., NaOH, CaOH, KOH, quarternary ammonium compounds; quantity required = 0.5 to 15% of phenol charge	Weak Bases, i.e., NH_3, primary, secondary and tertiary amines compounds; quantity required = 0.5 to 6% of phenol charge	Acids, i.e., formic, sulfuric, phosphoric, oxalic, etc.; quantity required = 0.1 to 2% of phenol charge
Method of Handling	Removed from reactor and cooled; maintained as a liquid	Condensation water vacuum-distilled off; redissolved in alcohol for most uses	Condensation water vacuum-distilled off; removed from reactor and solidifies when cooled; ground to fine powder or left in lumps; resin may be redissolved
General Properties	Water-soluble; dilutability = 100 parts water to 1 part resin	Slightly soluble in water; max. dilutability = 20 parts water to 100 parts resin	Solids are thermoplastic; resins are too brittle at room temperature

Table A.1 (*continued)*

Stability	Unstable; must be refrigerated prior to use to delay advance of final condensation polymerization	Unstable; must be refrigerated prior to use	Stable; some compositions have maximum shelf life of one week at 160ºC
Curing Requirements	Cures by heat or change of pH or both; acidic catalysts may be added	Cures by heat and low pressure or acid catalysts may be added	Requires addition of 10-15% hexamethylene-tetramine, formaldehyde or other methylol-group donor; becomes thermo-setting upon application of heat and high pressure
Typical Uses	Binders, coatings and casting	Industrial and decorative laminates, adhesives	Molding compounds, coated foundary sand and brake-lining binders

APPENDIX B

One Example for Flexural Stress versus Flexural Strain Curves of each Specimen

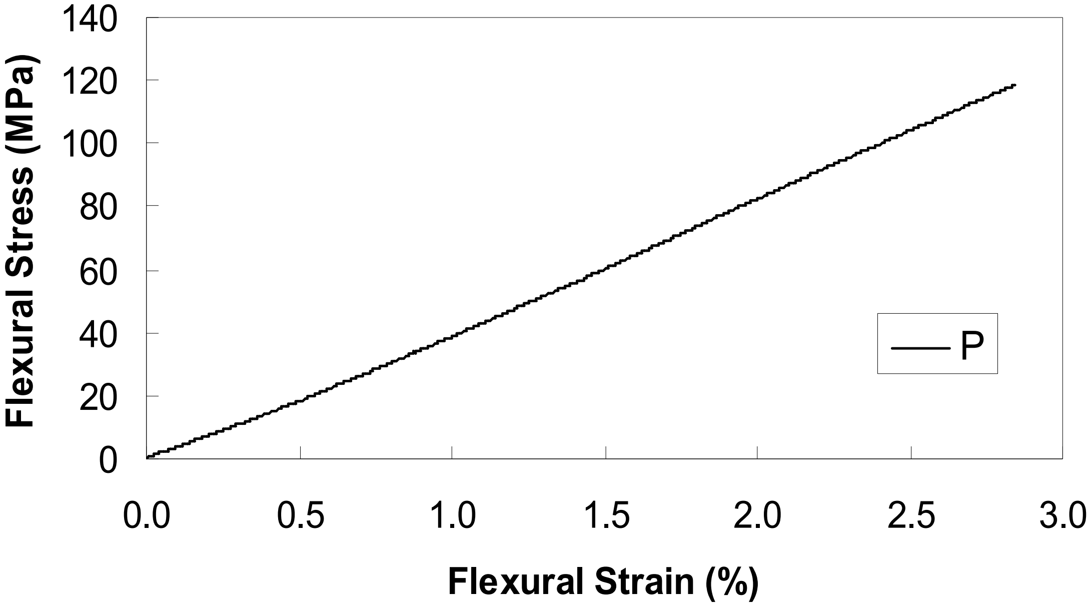

Figure B.1 For P specimen

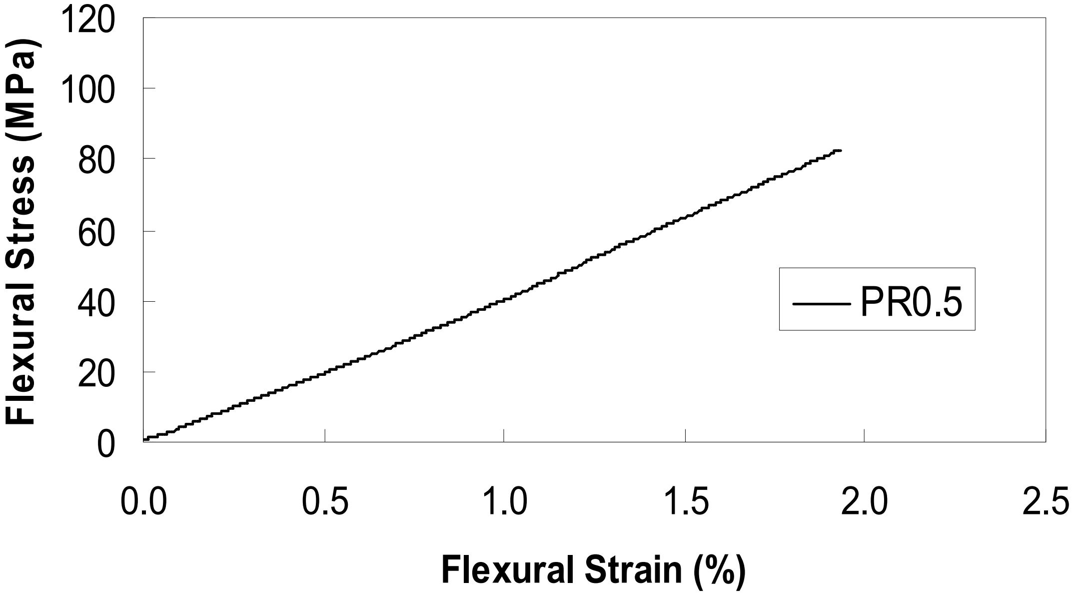

Figure B.2 For PR0.5 specimen

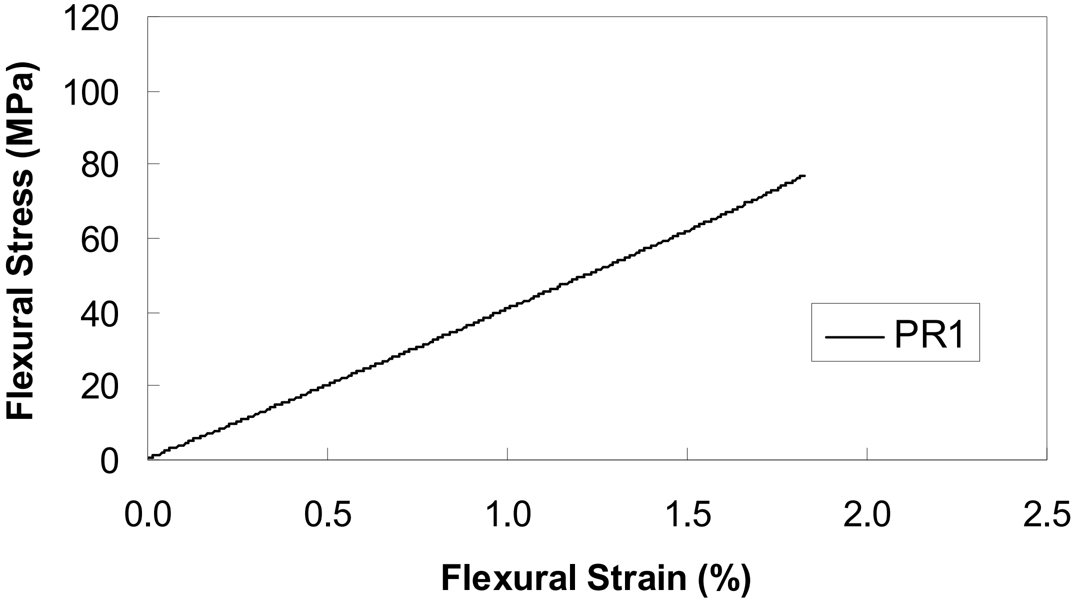

Figure B.3 For PR1 specimen

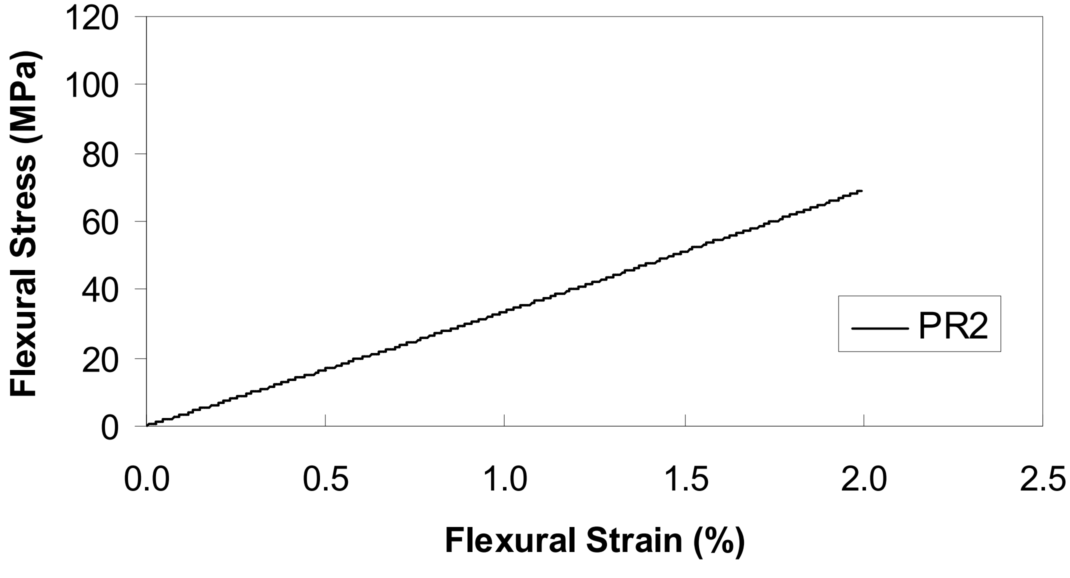

Figure B.4 For PR2 specimen

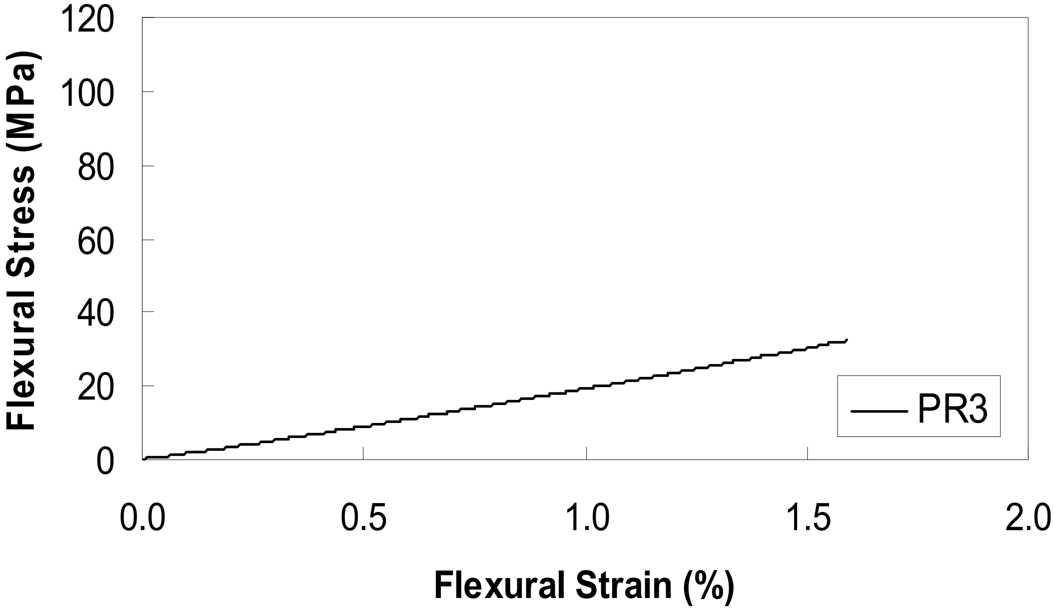

Figure B.5 For PR3 specimen

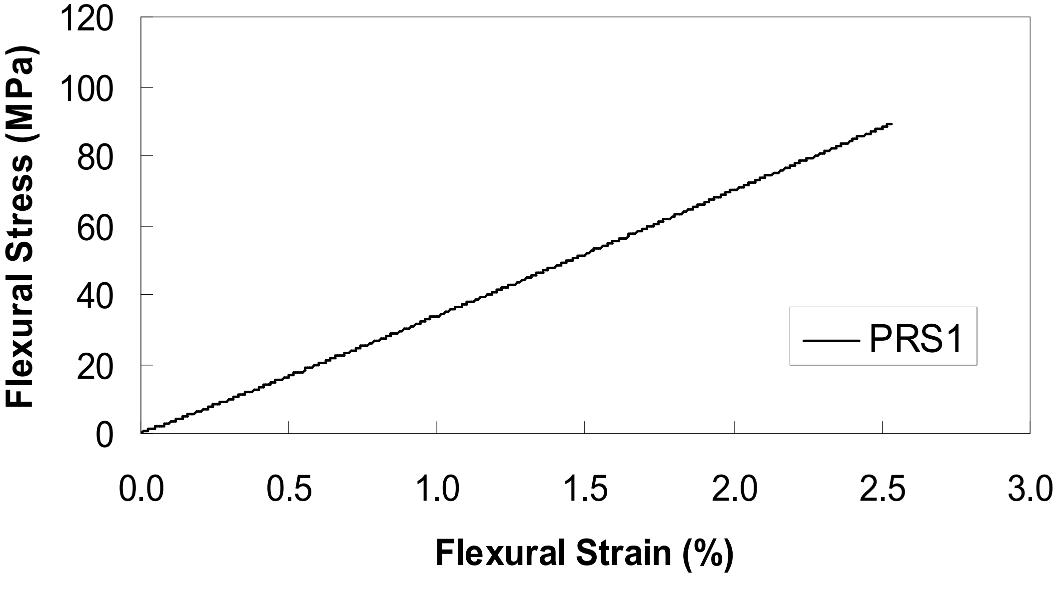

Figure B.6 For PRS1 specimen

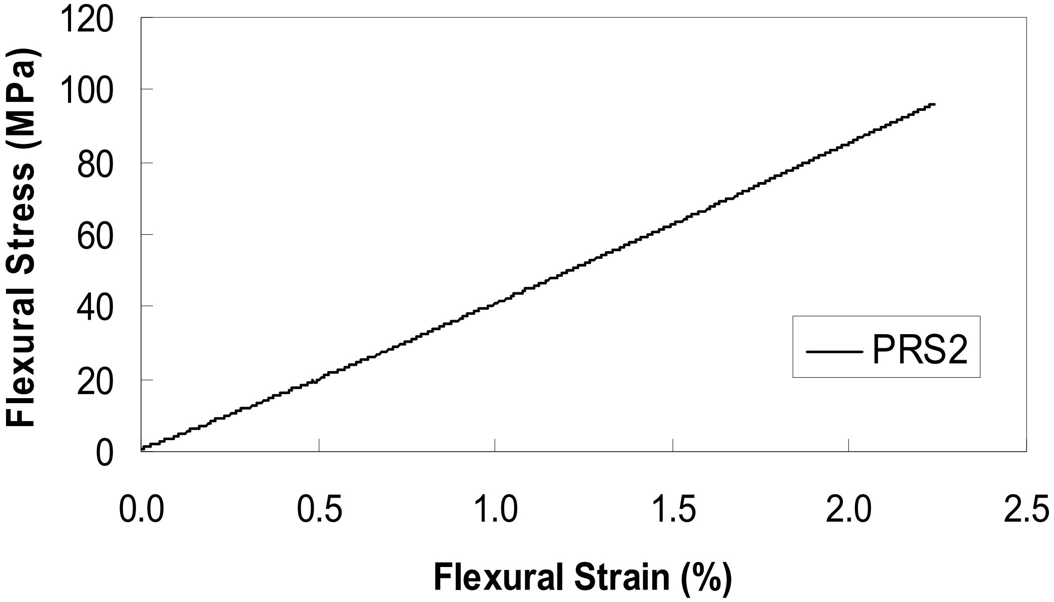

Figure B.7 For PRS2 specimen

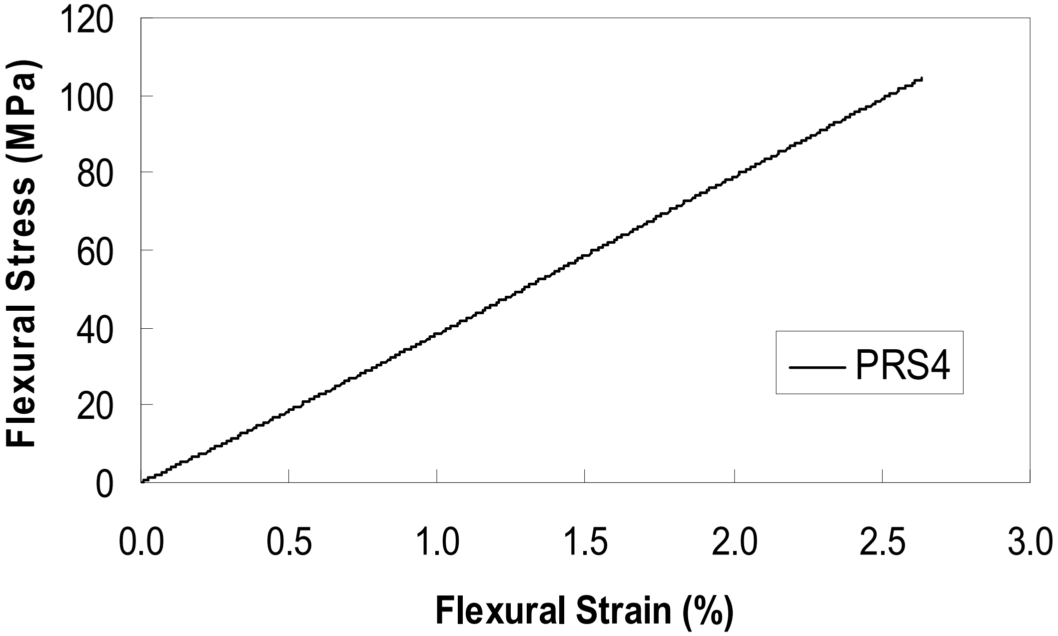

Figure B.8 For PRS4 specimen

APPENDIX C

One Example for Load versus Deflection Curves of each specimen used in Fracture Toughness Determination

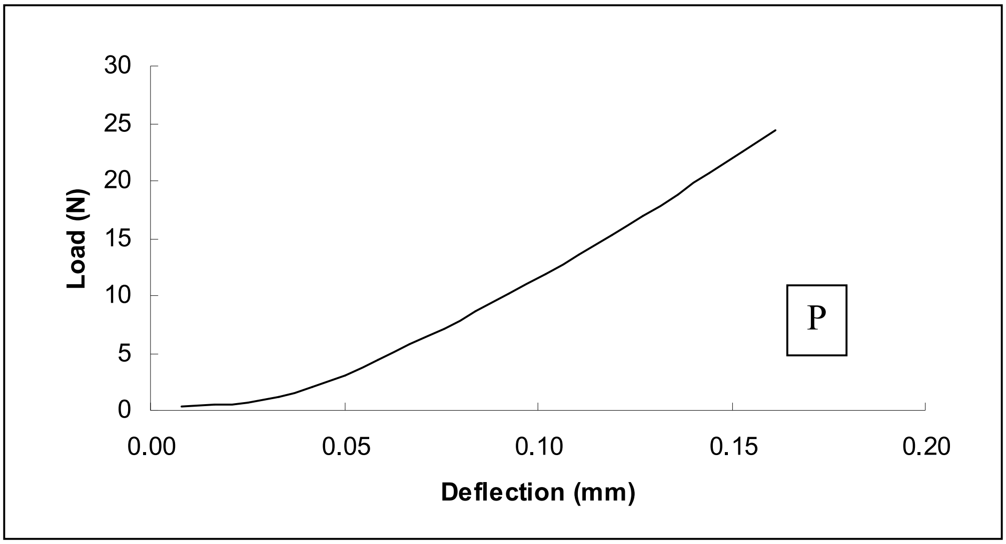

Figure C.1 For P specimen

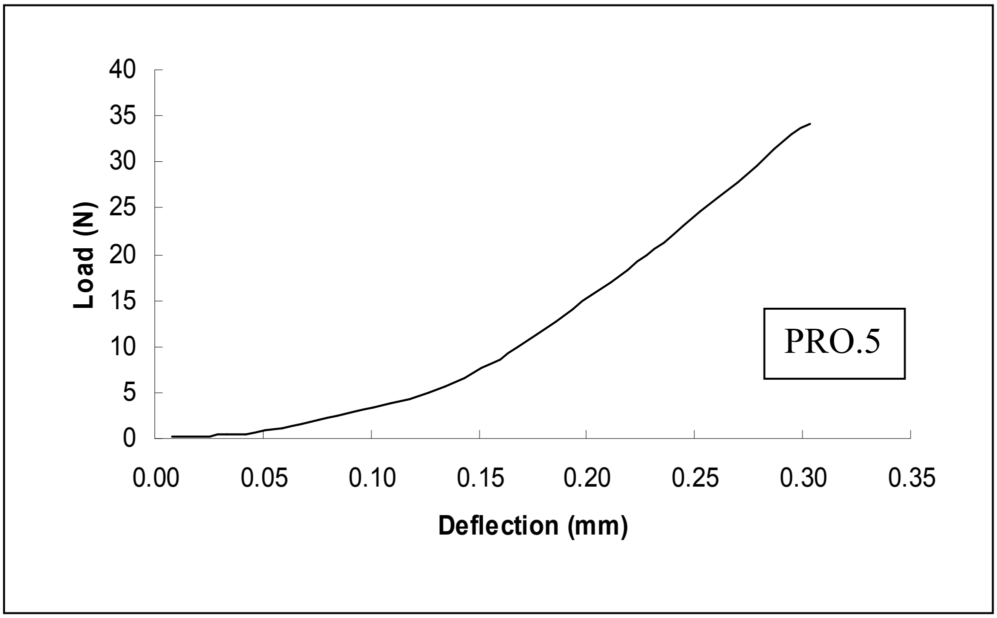

Figure C.2 For PR0.5 specimen

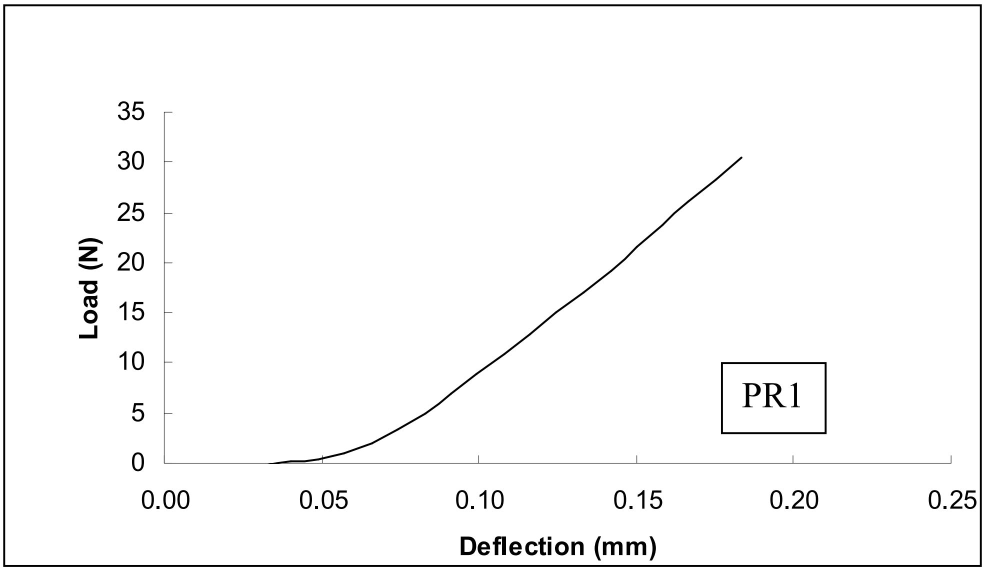

Figure C.3 For PR1 specimen

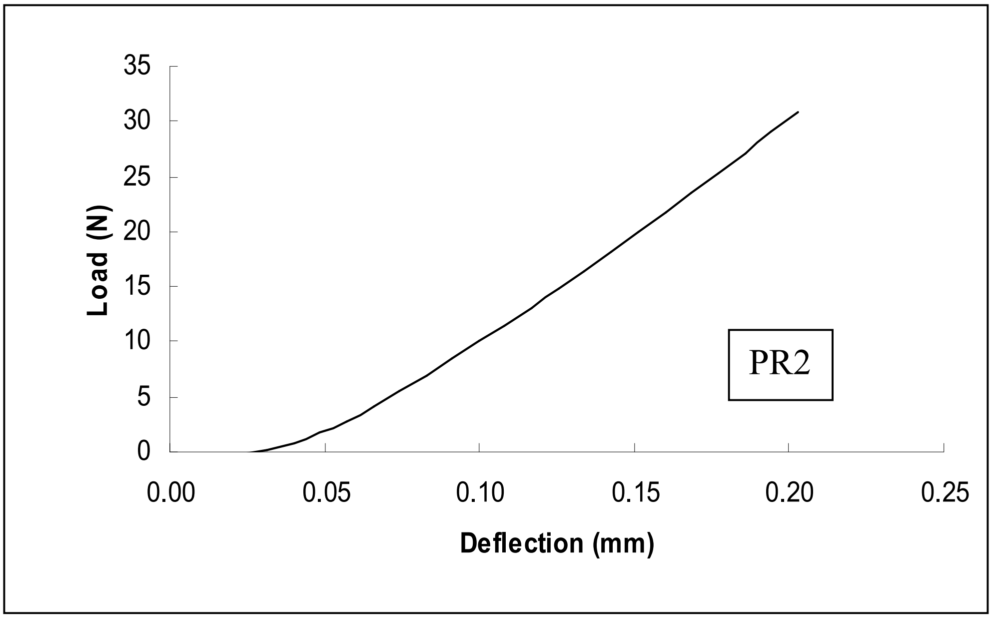

Figure C.4 For PR2 specimen

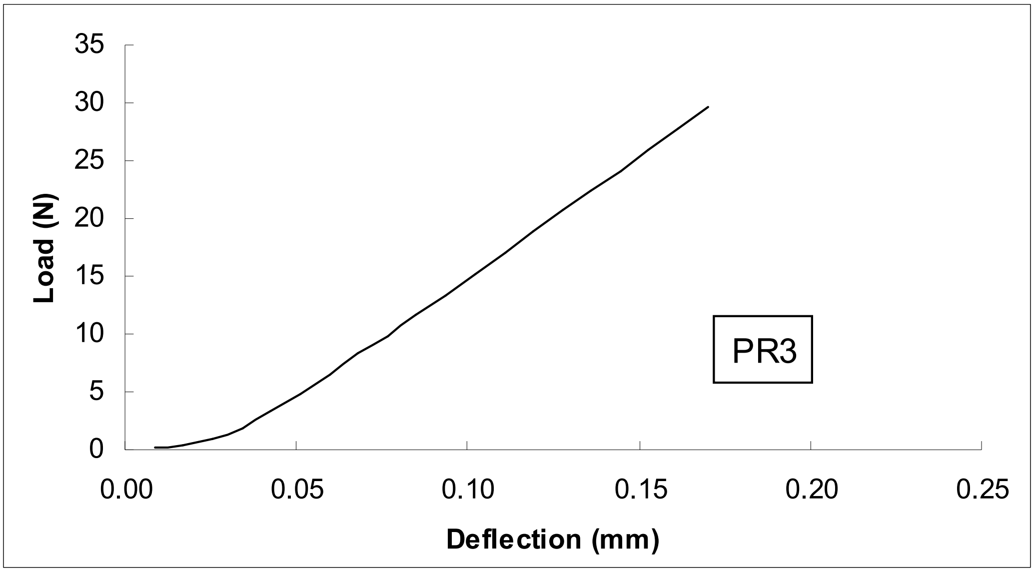

Figure C.5 For PR3 specimen

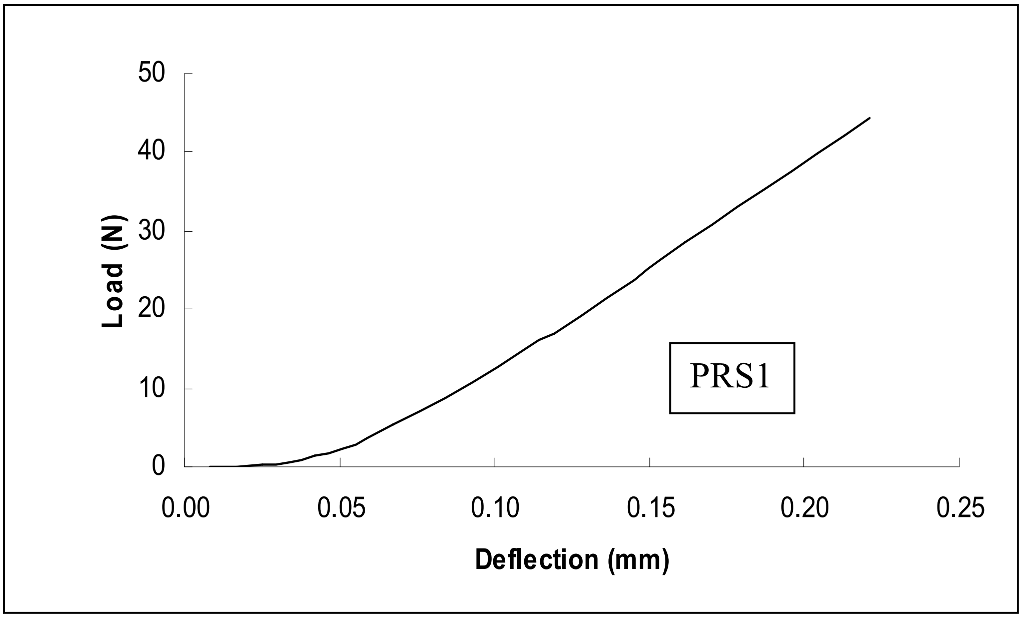

Figure C.6 For PRS1 specimen

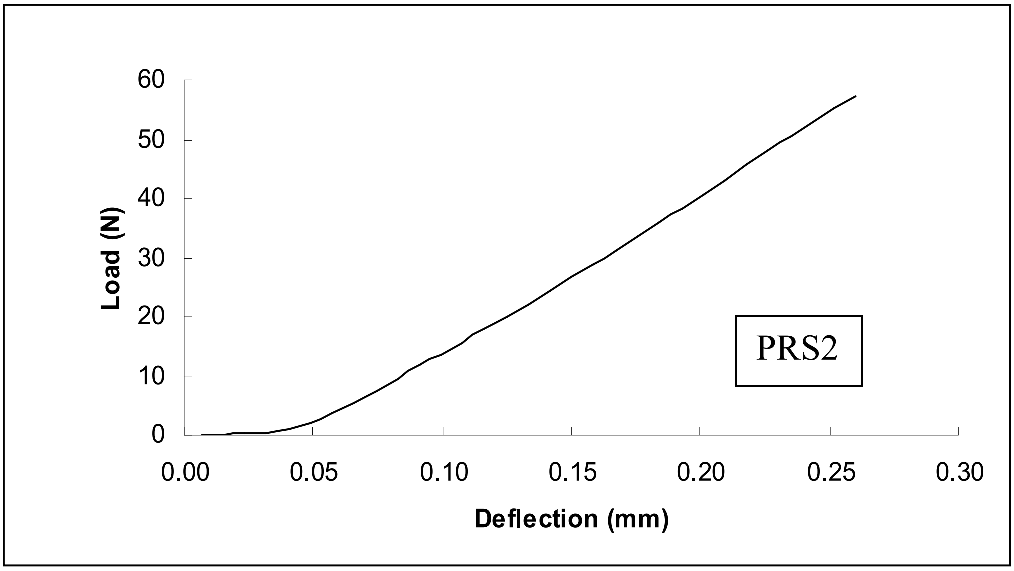

Figure C.7 For PRS2 specimen

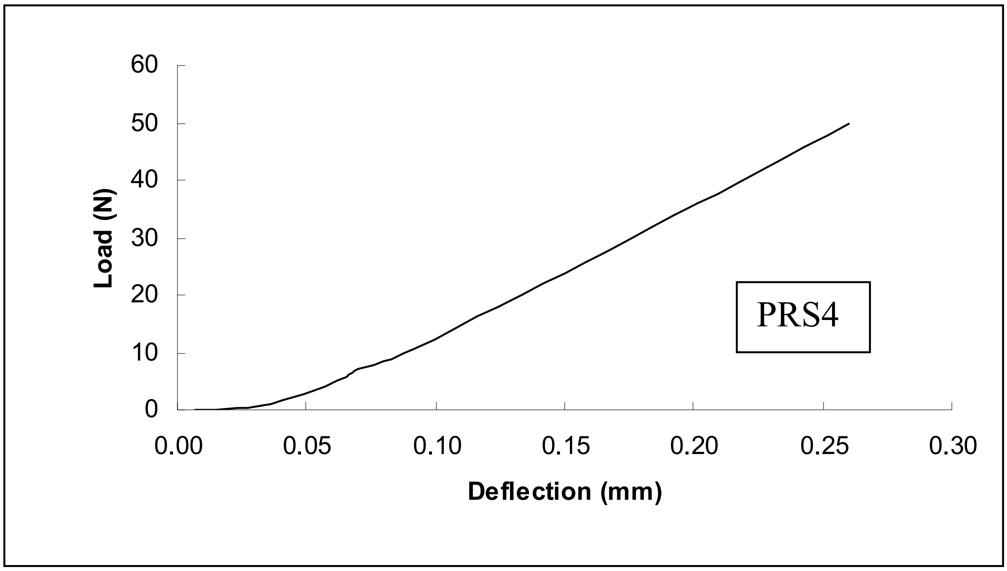

Figure C.8 For PRS4 specimen

APPENDIX D

Storage Modulus (*E'*) and Loss Tangent (*Tanδ*) versus Temperature curves of all Specimens

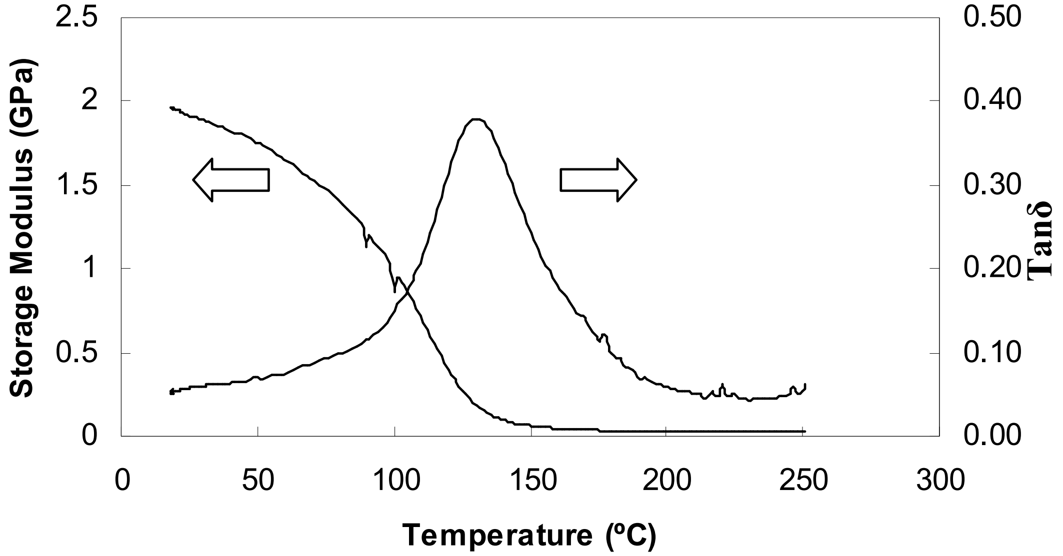

Figure D.1 For P specimen

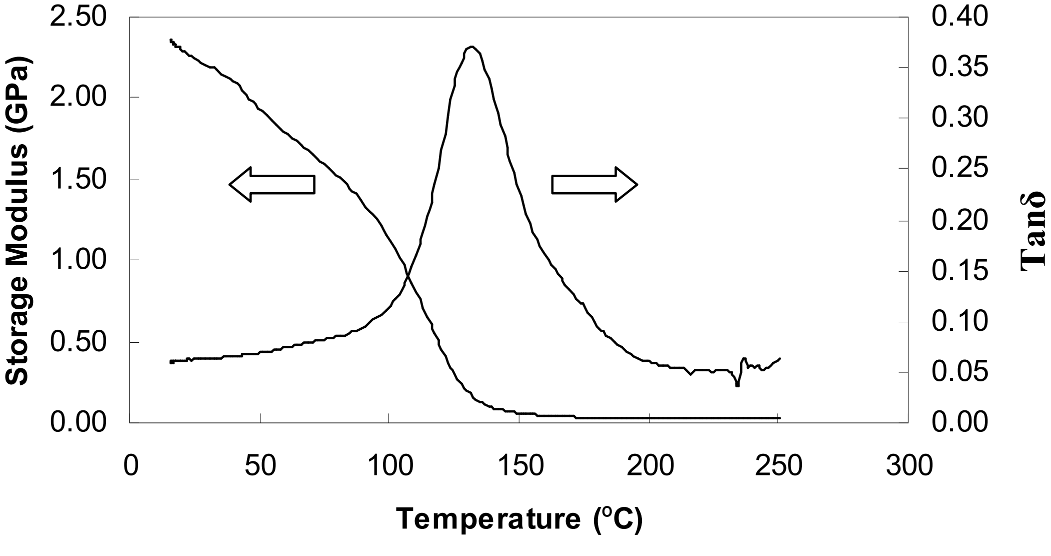

Figure D.2 For PR0.5 specimen

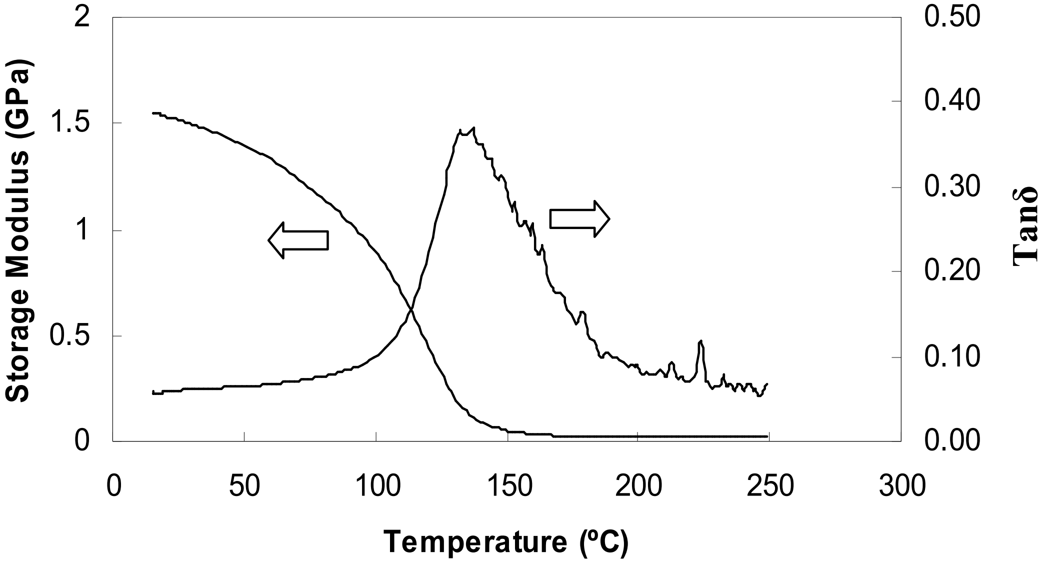

Figure D.3 For PR1 specimen

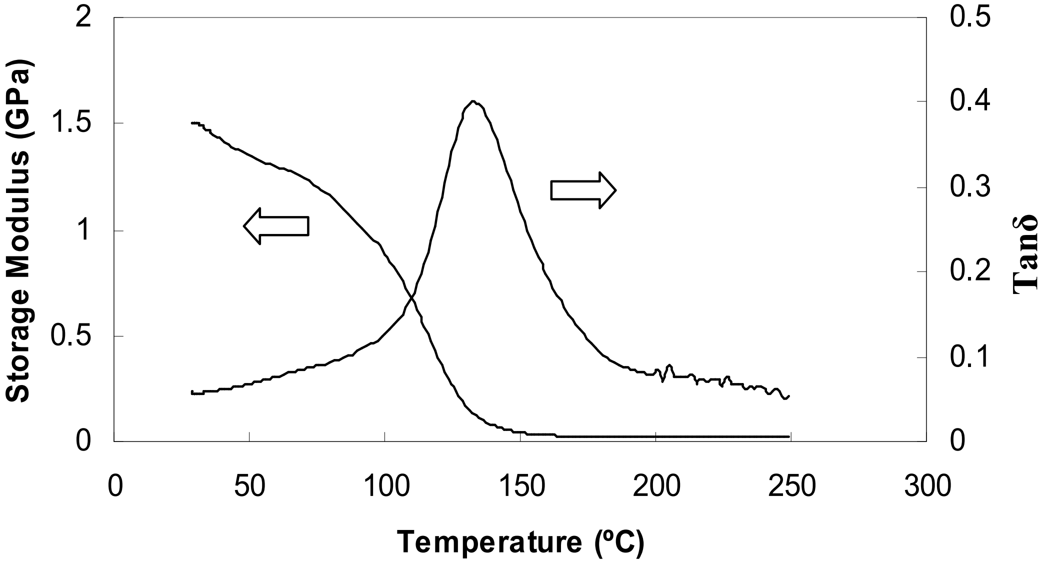

Figure D.4 For PR2 specimen

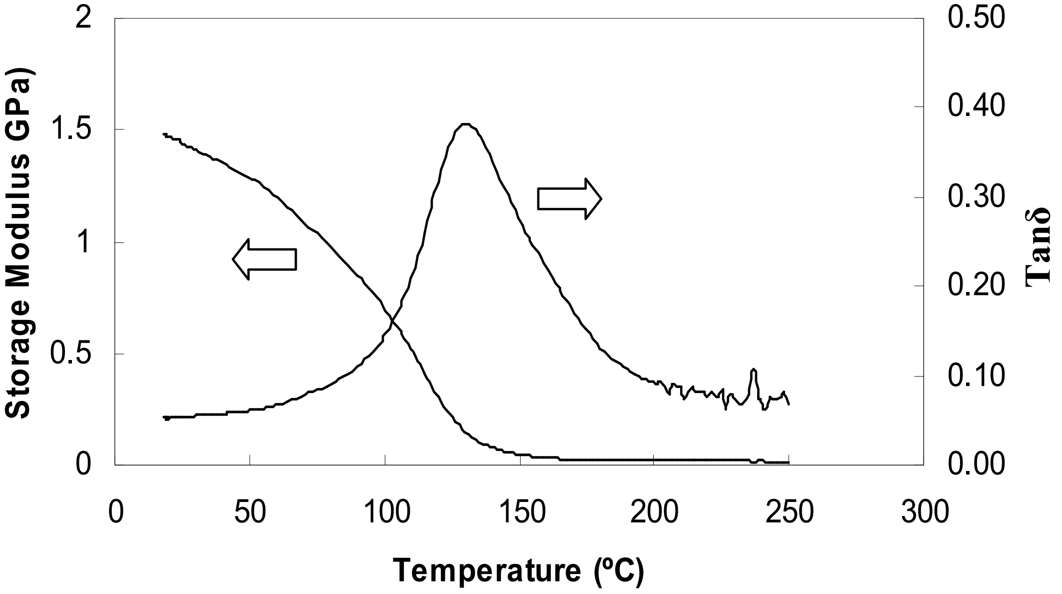

Figure D.5 For PR3 specimen

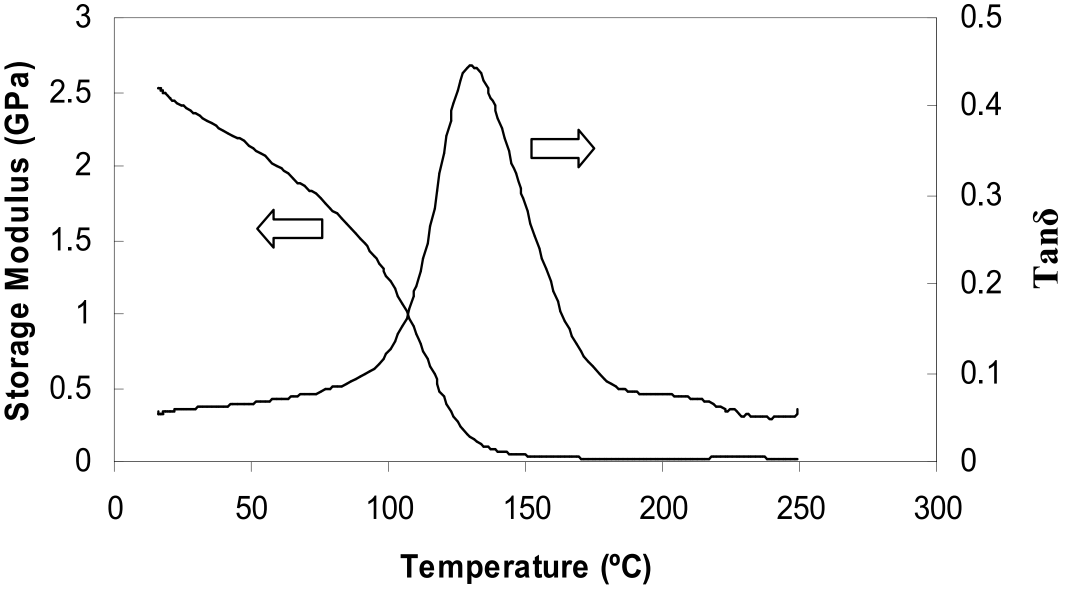

Figure D.6 For PRS1 specimen

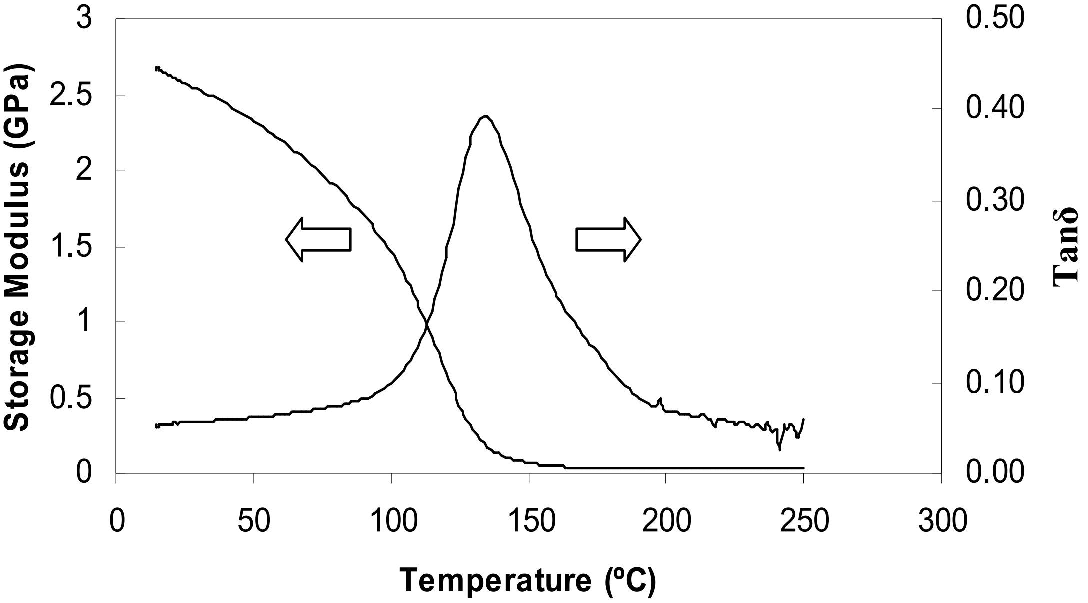

Figure D.7 For PRS2 specimen

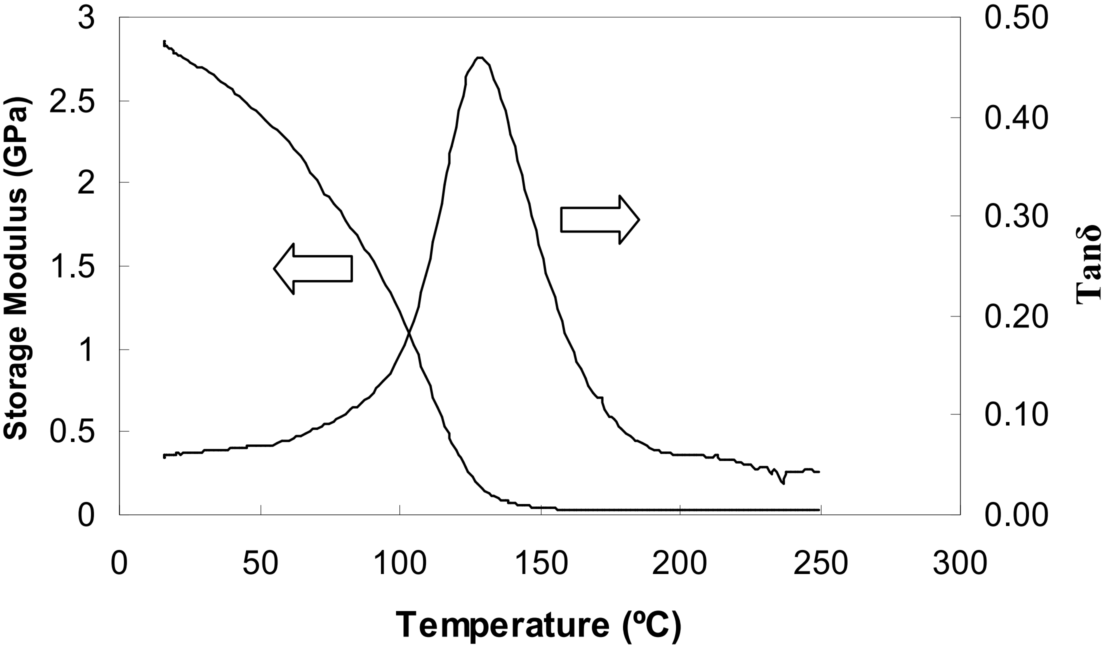

Figure D.8 For PRS4 specimen