

Influence of ABS Type on Morphology and Mechanical Properties of PC/ABS Blends

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SYNOPSIS

The morphology and the mechanical properties of polycarbonate (PC) blends with different acrylonitrile-butadiene-styrene (ABS) materials were investigated. PC/ABS blends based on a mass-made ABS with 16% rubber and large (0.5–1 μm) rubber particles are compared to blends based on an emulsion-made ABS with 50% rubber and small, monodisperse (0.12 μm) rubber particles over the full range of blend compositions. The blends with the bulk ABS showed excellent impact strength for most compositions, and those containing 50 and 70% PC exhibited ductile to brittle transition temperatures below that of PC. The blends with the emulsion ABS showed excellent toughness in sharp notch Izod impact tests at room temperature and in standard notch Izod impact tests at low temperatures near the T_g of the rubber. By melt blending the various ABS materials with a styrene-acrylonitrile (SAN 25) copolymer, materials with lower rubber concentrations were obtained. These materials were used in blends with PC to make comparisons at constant rubber concentrations of 5, 10, and 15%. The results of this investigation show that brittle ABS materials can produce tough PC-ABS blends. It is apparent that small rubber particles toughen PC-ABS blends at lower rubber concentrations and at lower temperatures than is possible with large rubber particles. However, additional work is needed to understand the nature of toughening in these PC-ABS blends with different rubber phase morphologies. It is of particular interest to understand the exceptional ductility of some of the blends at low temperatures. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polycarbonate (PC) blends with acrylonitrile-butadiene-styrene (ABS) materials are commercially important plastics that have been found to be useful in many molding applications, particularly in the automotive industry. These blends are successful because they economically combine some of the best properties of the components, e.g., excellent impact strength (including improved notch sensitivity and thick section toughness), high heat distortion temperature, and relatively low melt viscosity for improved processibility. Over the past 30 years, many patents have been issued covering PC-ABS blend technology. The first U.S. patent was issued to

Grabowski¹ in 1964. More recent U.S. patents cover various novel compositions, processes, and applications.²⁻¹⁵

There are two main types of ABS used in PC-ABS blends.¹⁶ Mass or bulk ABS is made by polymerizing styrene and acrylonitrile monomers in the presence of a dissolved butadiene-based rubber to which some grafting occurs. As the styrene-acrylonitrile (SAN) copolymer is formed, phase separation occurs followed by phase inversion, trapping some SAN within the rubber phase. The resulting rubber particles have SAN occlusions and are relatively large (0.5–1 μm). The amount of rubber that can be incorporated into mass-produced ABS is limited by viscosity to about 18% by weight. Emulsion-produced ABS is made by a two-step polymerization. First butadiene is polymerized to form a rubber; often it is a butadiene-based copolymer. Next styrene and acrylonitrile are polymerized in the

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presence of the butadiene-based rubber particles to produce the SAN-grafted rubber and the SAN matrix. The resulting rubber particles are typically small (0.1–0.5 μm), although larger particles with small SAN occlusions can be produced through variations of this process. The emulsion process can produce ABS materials with high rubber concentrations. Often these high rubber content materials are blended with SAN or other ABS materials to achieve desired properties by varying the rubber concentration and particle size distribution.

A number of studies have been published on PC blends with ABS.^{17–38} Also blends of PC with related materials such as SAN,^{36–52} methacrylate–butadiene–styrene (MBS) emulsion-made core-shell rubber modifiers,^{53–58} and other impact modifiers⁵⁹ have been investigated. Although several studies using commercial PC–ABS blends have been published,^{31,32,56} no direct comparisons of blends based on emulsion versus bulk ABS appear to be available.

PC–ABS blends exhibit excellent mechanical properties and provide processing advantages over pure polycarbonate. Several studies report on trends of impact strength and break strain with respect to blend composition.^{17–19,22,23,29,30,35,37} The observed differences in properties can be attributed in part to ABS rubber composition and ABS rubber particle type. Other factors affecting the phase morphology and mechanical properties of PC–ABS and related blends include PC molecular weight,³⁵ processing conditions,^{26,27,34,56} and thermal history.^{50,51,54,55} Some reports have focused on the fracture mechanisms of PC–ABS and related blends, concluding that both cavitation processes and shear yielding are involved.^{24,28,31,37–39,41,45,48,49,53,58} Test variables that can affect the mechanical behavior include strain rate, temperature, section thickness, and notch radius. Variables affecting the intrinsic toughness of a blend include composition, the component molecular weight and properties, the domain size and size distribution, molecular orientation, and the interfacial adhesion and molecular interactions between the phases. Interfacial adhesion, resulting from the segmental interactions between the PC and SAN phases, is of critical importance in PC–ABS blend toughening. Polycarbonate and SAN have been reported to be partially miscible based on observed shifts in the T_g 's of the individual phases and on theoretical calculations,^{38,46} but recently it has been shown that the partial miscibility is limited, and the shifts in T_g 's can be mostly attributed to oligomers partitioning between the SAN and PC phases.^{40,43,45} The interfacial adhesion between PC and SAN has

been found to be maximum at approximately 25% AN in SAN,^{40,45,46} which interestingly is close to that used in most ABS materials. The level of PC–SAN interfacial adhesion is sufficient such that useful products can be formed without the aid of any compatibilizer contrary to experience with blends of ABS with other polymers like nylon or polyester.

The purpose of this study is to investigate the morphology and the mechanical properties of PC–ABS blends based on different types of ABS materials. First, binary blends of PC with SAN 25 and two ABS materials representing extremes in rubber content and rubber particle type are considered, viz., a bulk-made ABS with 16% rubber and an emulsion-made ABS with 50% rubber. PC–SAN 25 blends show the limiting case of 0% rubber content in the ABS. The effect of rubber particle type in ABS is examined by comparing blends of PC with three different materials where the rubber contents have been made equal by dilution with SAN 25. At each PC–ABS blend ratio, the mechanical properties are presented as a function of rubber content in the ABS phase. This approach allows some comparisons between different rubber particle sizes and distributions.

EXPERIMENTAL

Materials

Table I describes the materials used in this study and gives their melt rheological characteristics. Rheological properties of PC–ABS blends have been described more fully elsewhere.^{17,18,21,35,36} Torque measurements were recorded at 270°C and 60 rpm in a Brabender Plasticorder with a 50-mL head and standard rotors. Calibre 200-3 is a high-molecular-weight polycarbonate, chosen to provide the best mechanical properties and to minimize the effects of degradation that might occur during processing. Magnum 541 (ABS 541) is a bulk-produced material containing 16% rubber by weight. The rubber particles in ABS 541 are polydisperse and typically 0.5–1 μm in diameter. DP-611 (ABS 611) and graft rubber concentrate (GRC) (ABS GRC) are emulsion-produced ABS materials containing 40 and 50% rubber, respectively. The rubber particles in ABS 611 are polydisperse comprising mostly small particles (0.1–0.3 μm in diameter) with some larger ones (approximately 1 μm in diameter) that contain SAN occlusions. The rubber particles in ABS GRC are relatively monodisperse and small (0.12 μm diameter). Tyril 1000 (SAN 25), a high-molecular-weight

Table I Materials Used in This Study

Polymer	Designation	Description	Composition ^a	Molecular Weight ^b	Brabender ^c Torque (N·m)	Source
PC	Caliber 200-3	Polycarbonate of bisphenol A, MFI = 3	—	$\bar{M}_n = 13,400$ $\bar{M}_w = 36,000$	16.4	Dow Chemical Co
ABS 541	Magnum 541	Mass-produced ABS	16% rubber	$\bar{M}_n = 59,000$	3.6	Dow Chemical Co.
ABS 611	DP-611	San-grafted emulsion rubber, polydisperse	25% AN in SAN 40% rubber 25% AN in SAN	$\bar{M}_w = 140,000$ n.a.	10.5	Japan Synthetic Rubber
ABS GRC	GRC	SAN-grafted emulsion rubber, monodisperse	50% rubber 25% AN in SAN	n.a.	18.2	Dow Chemical Co.
SAN 25	Tyrl 1000	Styrene-acrylonitrile copolymer	25% AN	$\bar{M}_n = 77,000$ $\bar{M}_w = 152,000$	2.4	Dow Chemical Co.

^a Weight %.^b n.a. = not available.^c Brabender torque recorded after 20 min at 270°C and 60 rpm.

copolymer containing 25% AN, was chosen to lower the rubber concentration in ABS to a desired level. The SAN component of each ABS material contains close to 25% AN, assuring miscibility with SAN 25.^{60,61} The ABS materials were selected from those available after completing a series of exploratory blends to determine their chemical compatibility with PC.⁶²

Blend Preparation

Low rubber content ABS materials were made by blending ABS with SAN 25. The ABS pellets of reduced rubber concentration were then molded into test specimens or blended with PC. The PC-ABS blends were prepared by blending PC with either a virgin ABS or an ABS preblend; no blends were made by simultaneous mixing of the three components. Blends were prepared by melt mixing in a Killion single-screw extruder ($L/D = 30$, 2.54 cm diameter). Prior to melt blending or injection molding all polymers were dried in a vacuum oven overnight at 75°C. Test specimens for mechanical property evaluation were produced using an Arburg All-rounder 305 screw injection molding machine. ABS-SAN 25 blends were processed at 180°C unless otherwise noted, and PC-ABS and PC-SAN blends were processed at 270°C (mold temperature = 65°C). Other molding parameters were held constant for all blends.

Mechanical Testing

Izod impact testing was performed using a pendulum-type tester. The impact strength data represent average values of at least four test specimens. Standard deviations for these data are typically $\pm 5\%$, but the variability is greater in ductile to brittle transition regions. Standard notch test bars (thickness = 3.18 mm) conformed to ASTM D 256. Sharp notch specimens were prepared by pressing a new razor blade into the center of the machined standard notch. Low-temperature impact testing was performed on bars with standard notches. Liquid carbon dioxide was used to cool the bars, and a thermocouple implanted in a neighboring test specimen was used to monitor the temperature. Tensile tests were performed using an Instron model 1137, using specimens that conformed to ASTM D 638 type I. Modulus values were determined using a 25-mm extensometer and a crosshead speed of 5 mm/min. Tensile strength and break strain measurements were made at a crosshead speed of 50 mm/min. The tensile data represent average values of at least four test specimens. Standard deviations for the modulus data are typically $\pm 5\%$, but for some materials the standard deviations might be as high as $\pm 10\%$. Standard deviations for the tensile strength data are typically less than $\pm 5\%$. The break strain data is more variable, especially for highly ductile blends. Many of the PC-rich blends exhibited break strains ranging

from 25 to 140%. The low values for these specimens might be attributed to imperfections that cause a premature failure.

Microscopy

Ultrathin sections for transmission electron microscopy (TEM) were prepared using a Reichert-Jung Ultracut E microtome having a diamond knife and equipped for cryogenic operation. The details of this procedure have been given elsewhere.⁶³ Sections were taken from the center of an injection-molded bar in a plane perpendicular to the direction of flow. When microtoming ABS materials, the specimen temperature was set to -40°C . When microtoming PC-SAN or PC-ABS blends, the specimen temperature was set to -10°C . The knife temperature was set to -45°C for all samples. Sections of ABS materials were vapor stained for 18 h over a 4% aqueous solution of osmium tetroxide (OsO_4). The OsO_4 -stained rubber particles appear black in TEM. Sections of PC-SAN blends were vapor stained for 8 min over a 0.5% aqueous solution of ruthenium tetroxide (RuO_4). The RuO_4 -stained PC appears gray in TEM photomicrographs. Sections of PC-ABS blends were first exposed to OsO_4 then to RuO_4 as described above. The SAN phase remains unstained in this procedure. This dual staining technique allows simultaneous viewing of the PC, SAN, and rubber phases. The RuO_4 was allowed to warm to room temperature before staining because temperature seemed to affect staining time. Finding the optimal staining time is critical when using RuO_4 to avoid artifacts from overstaining. A JEOL 200 CX transmission electron microscope was used.

EFFECT OF ABS TYPE IN PC-ABS BLENDS

The morphology and mechanical properties of binary blends of PC with two ABS materials, ABS 541 and ABS GRC, and SAN 25 were determined. Polycarbonate blends with these three materials represent extremes in rubber concentration and rubber particle type and might provide some insight into how these variables affect the behavior of PC-ABS blends. The effect of rubber concentration in ABS on PC-ABS blend properties will be considered later.

Morphology

Figure 1 shows TEM photomicrographs for three PC-SAN 25 blends. In the photomicrographs, the

PC phase appears gray, the rubber particles appear black, and the SAN phase remains unstained. Polycarbonate forms the continuous phase in the 90/10 and the 70/30 compositions, and PC and SAN 25 form an apparently co-continuous phase structure in the 50/50 blend. It should be noted that PC is approximately seven times as viscous as SAN 25 at 270°C . In the PC-rich blends the shapes of the SAN 25 domains are elliptical with smooth boundaries. In the 90/10 blend, the diameter of the SAN 25 domains ranges from 0.1 to $0.5\ \mu\text{m}$, and at the 70/30 composition, larger SAN 25 domains ($1\text{--}5\ \mu\text{m}$) are found, although a notable population of small domains ($0.1\text{--}0.5\ \mu\text{m}$) is also present throughout the PC phase. Some small SAN domains also are present in the PC phase at the 50/50 composition. The black specks in the PC phase of the 50/50 blend are staining artifacts caused by overexposure to RuO_4 .

Figure 2 shows photomicrographs for three PC-ABS 541 blends. Polycarbonate appears to form the continuous phase in the 90/10 and the 70/30 compositions, but PC and ABS 541 form a co-continuous morphology in the 50/50 blend. In these blends the shapes of the ABS domains are elliptical with smooth boundaries. The rubber particles are contained within the ABS domains, surrounded by a clearly visible layer of SAN. In addition to the larger ABS domains, small SAN domains without rubber particles are present in the blends. At the 90/10 and the 70/30 compositions, the ABS 541 domains appear to be larger than the domains in blends with SAN 25.

Figure 3 shows photomicrographs for three PC-ABS GRC blends. Polycarbonate forms the continuous phase at the 90/10 and the 70/30 compositions, but an apparent co-continuous morphology is formed in the 50/50 mixture. For these blends, the rubber particles appear agglomerated, and the ABS domains have irregular shapes and jagged boundaries. The possible reasons for rubber particle agglomeration will be discussed later. Also, because ABS GRC has a high rubber content, the rubber particles appear to fill the dispersed SAN domains, and the SAN component is difficult to see in the photomicrographs. The small SAN domains without rubber particles do not appear to be present in these blends.

Tensile Properties

Figure 4 shows the tensile modulus of PC blends with SAN 25, ABS 541, and ABS GRC. The blend moduli are intermediate to those of the pure components, and only small deviations from additivity

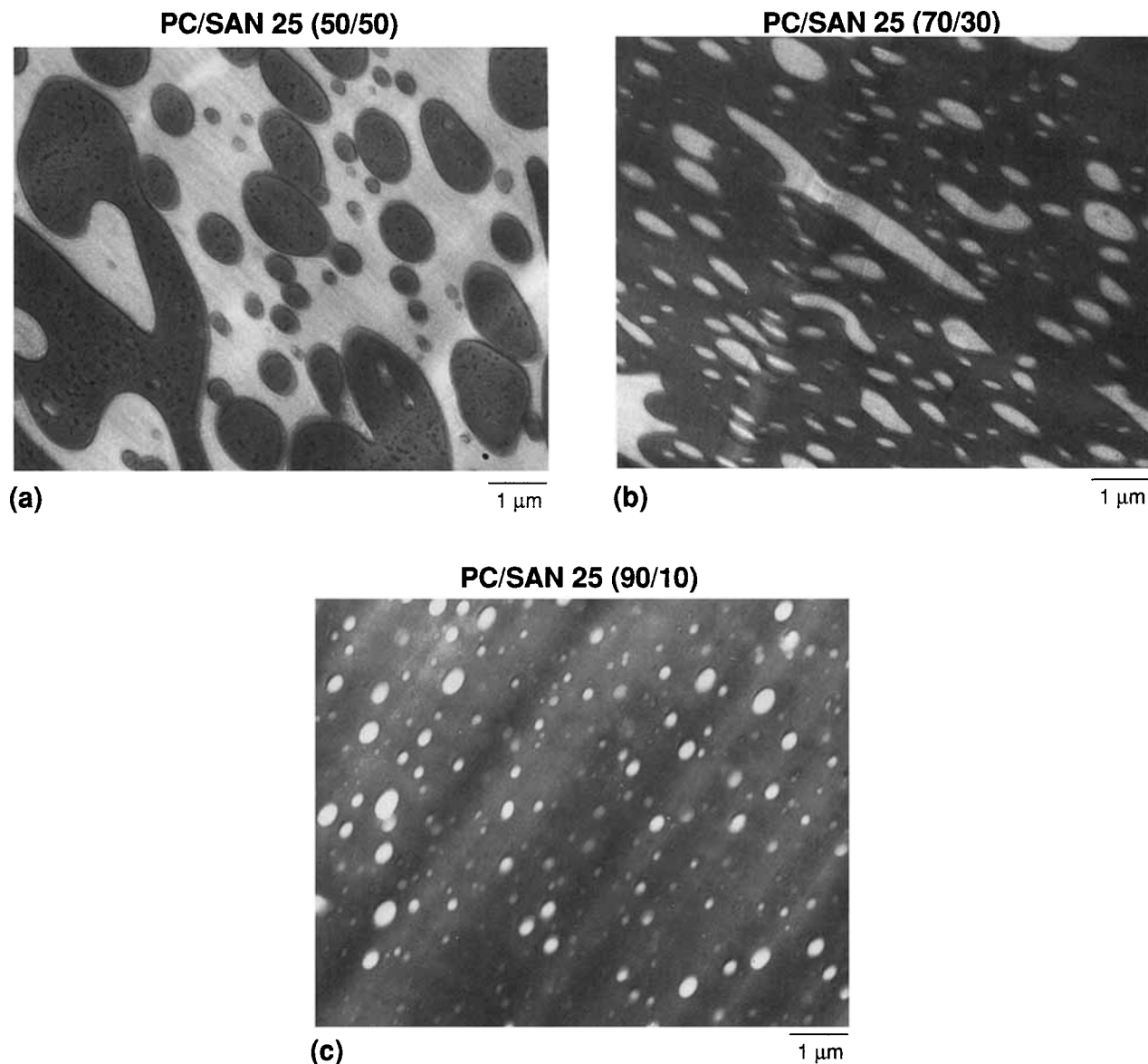


Figure 1 TEM photomicrographs of PC-SAN 25 blends at three compositions: (a) 50/50, (b) 70/30, and (c) 90/10.

are noted. The modulus of ABS 541 is similar to that of PC, but SAN 25 is more rigid and ABS GRC is more flexible. The modulus of ABS materials is related primarily to their rubber content.

Figure 5 shows the tensile strength of PC blends with SAN 25, ABS 541, and ABS GRC. All values shown are yield strengths except for PC-SAN 25 compositions of 0/100, 10/90, and 30/70, which did not yield before fracture. For the PC-SAN 25 blends, the tensile strength curve is complex in shape. Similar data have been published by Keitz et al.⁴⁶ For the PC-ABS blends, the tensile strength is nearly linear with respect to blend composition.

Figure 6 shows the strain at break for these blends. For the PC-SAN 25 blends, the break strain remains comparable to that of SAN 25 (about 5% elongation at break) at compositions with less than 30% PC and then gradually increases to the level of PC (about 100% elongation at break) at compositions with greater than 70% PC. Similar responses are seen for the blends with the two ABS materials. ABS GRC exhibits a much higher strain at break than ABS 541, but the latter is about twice that of SAN 25.

The results presented here are significantly different from those of Suarez et al.³³ where the break

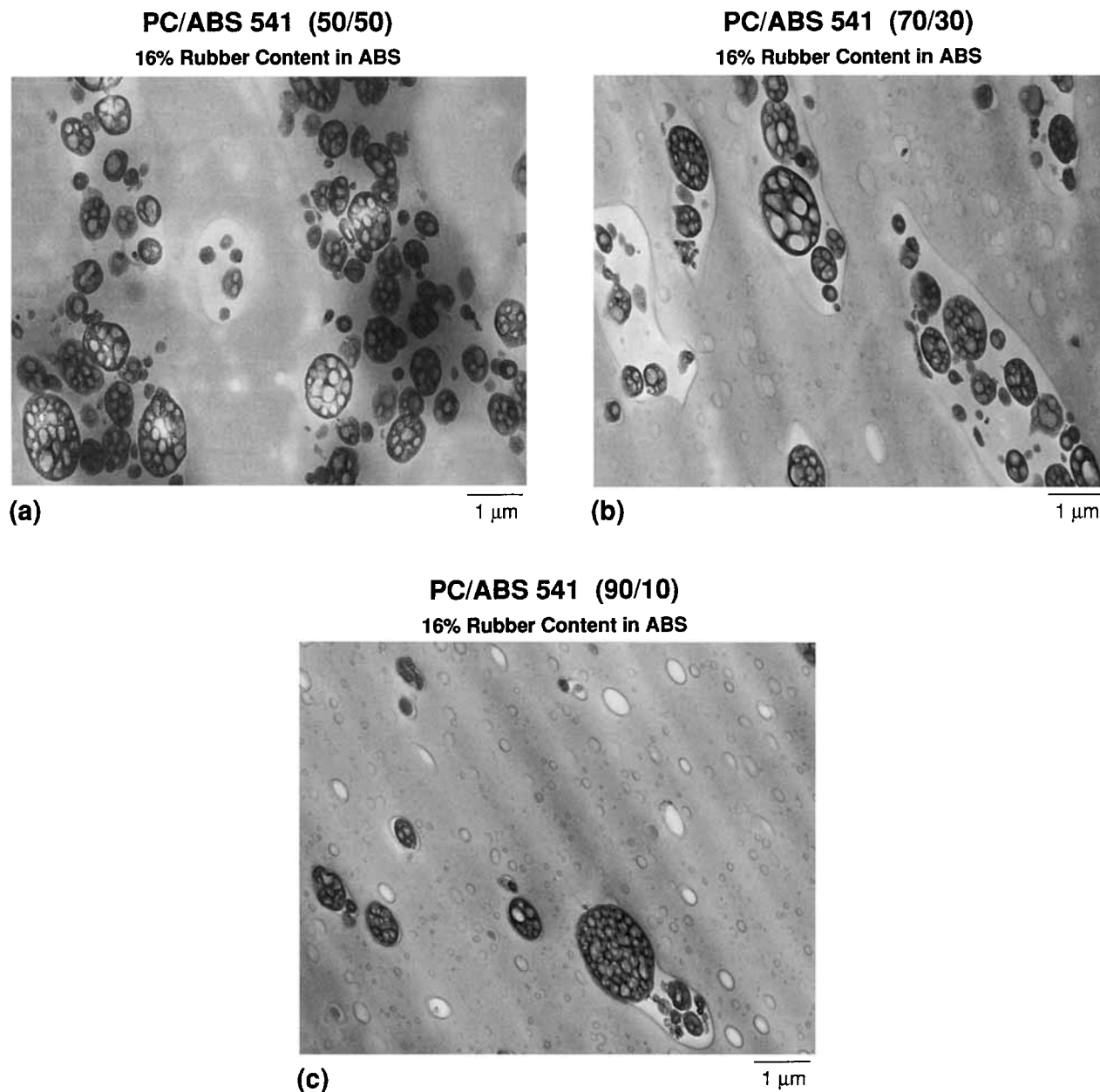


Figure 2 TEM photomicrographs of PC-ABS 541 blends at three compositions: (a) 50/50, (b) 70/30, and (c) 90/10.

strain for a series of PC-ABS blends was observed to be far below additivity and exhibited a minimum between 25 and 50% PC content. The details of the ABS material used by Suarez et al.³³ were not reported; but the PC used had a similar molecular weight to that used here.

Impact Properties

Standard notch Izod impact strength data for the same series of blends are shown in Figure 7. In the

PC-SAN 25 blends, the impact strength remains below 200 J/m for blends comprising less than 85% PC, then it increases sharply to about 1000 J/m at 90% PC and shows a slight maximum between 90 and 100% PC, as others have reported.⁴⁸ The impact strength for blends of PC with ABS 541 shows rather complex behavior. The impact strength remains comparable to ABS 541 (250 J/m) for compositions with less than 20% PC, although a slight minimum is observed at 10% PC. The impact strength increases to an exceptionally high level of about 800

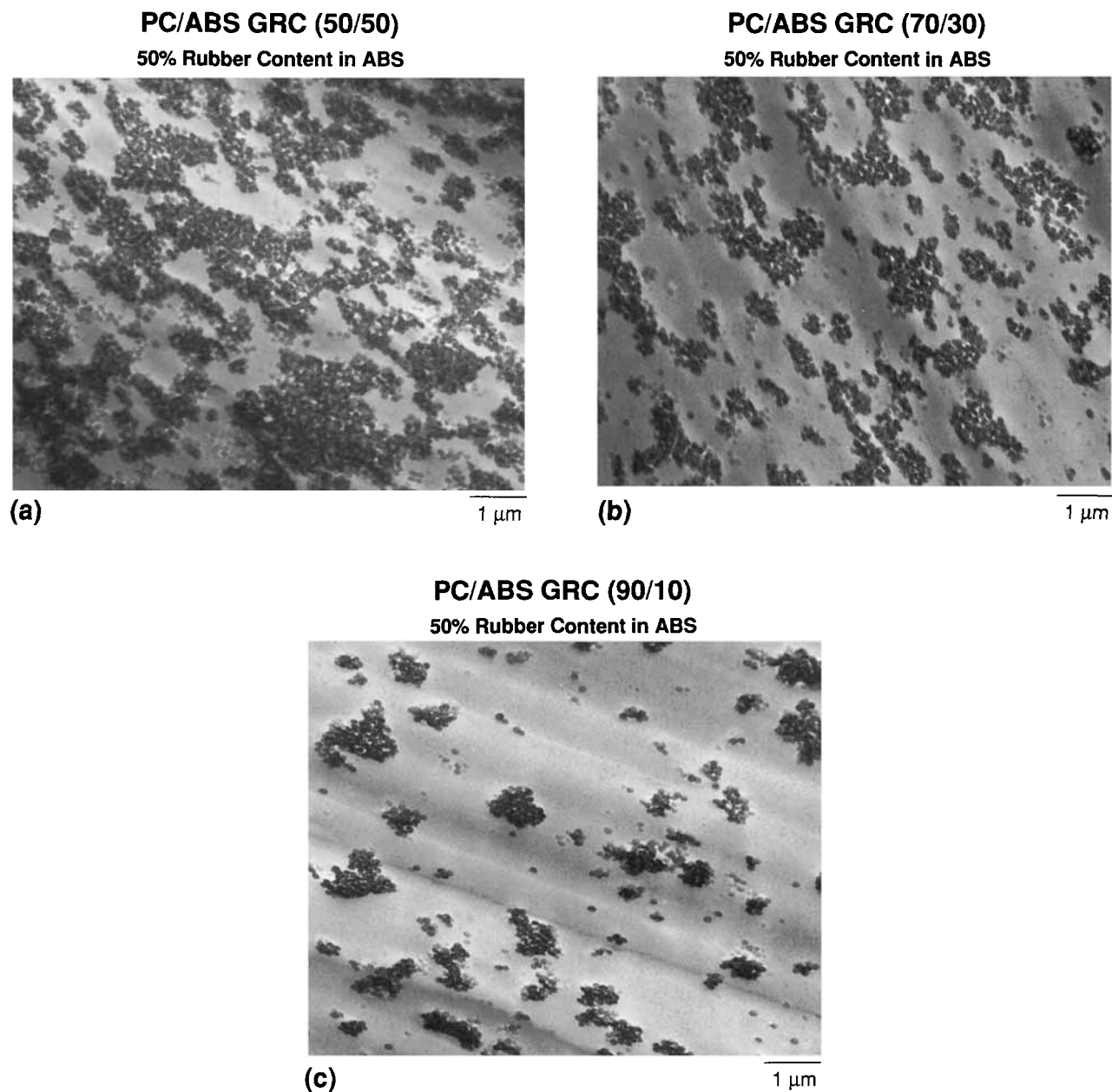


Figure 3 TEM photomicrographs of PC-ABS GRC blends at three compositions: (a) 50/50, (b) 70/30, and (c) 90/10.

J/m for compositions with greater than 40% PC, with a slight suggestion of a maximum at 90% PC. The impact strength for PC blends with ABS GRC increases monotonically from 350 J/m for ABS GRC to 1000 J/m for PC. At PC concentrations greater than 30%, the blends with ABS 541 are slightly tougher than those with ABS GRC, and at PC concentrations less than 30%, the blends with ABS GRC exhibit higher impact strengths than those with ABS 541. The latter appears to reflect the

toughness of the ABS continuous phase. Again, these results differ from those reported by Suarez et al.³³

Polycarbonate shows high notched Izod impact strength in thin sections with standard notches (notch radius = 0.25 ± 0.05 mm), but it is brittle for thicker sections (> 6.2 mm) and for sharp notches (e.g., formed by a razor blade). Figure 8 shows the differences in impact strength for specimens with standard versus razor-sharpened notches

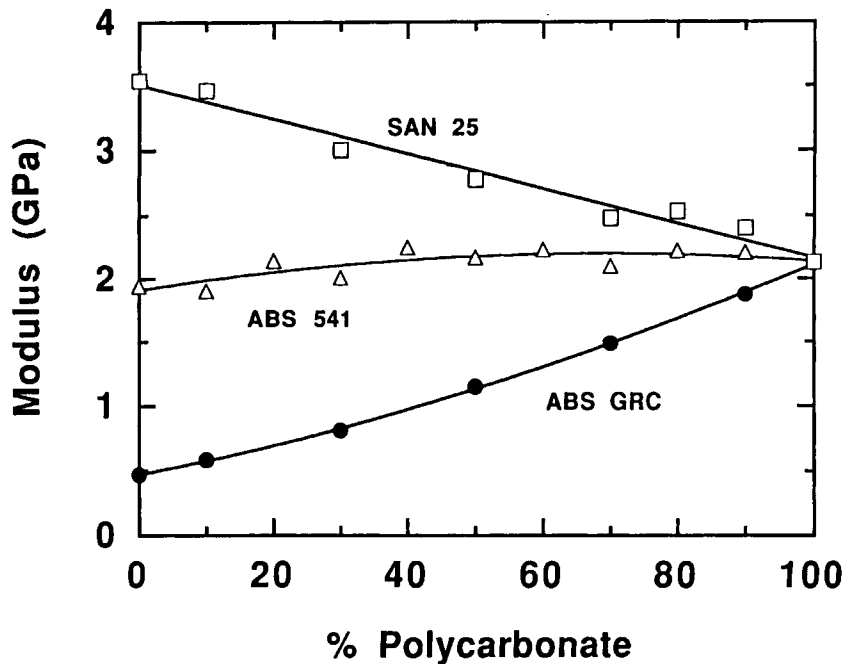


Figure 4 Tensile modulus of PC blends with SAN 25, ABS 541, and ABS GRC.

formed from blends of PC with the two ABS materials. PC-SAN 25 (not shown) is not tough at any composition in a sharp notch impact test. Blends of

PC with ABS 541 show that sharp notch impact strength is improved as more ABS is incorporated into the blend. A blend of PC with 10% ABS 541

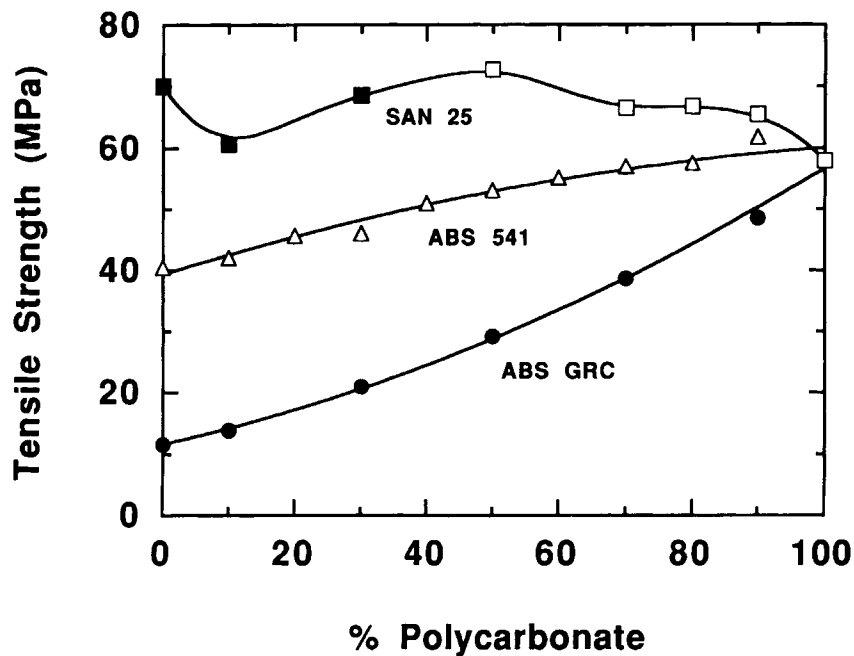


Figure 5 Tensile strength of PC blends with SAN 25, ABS 541, and ABS GRC. All values are yield stresses except those denoted by (■), which are ultimate stresses.

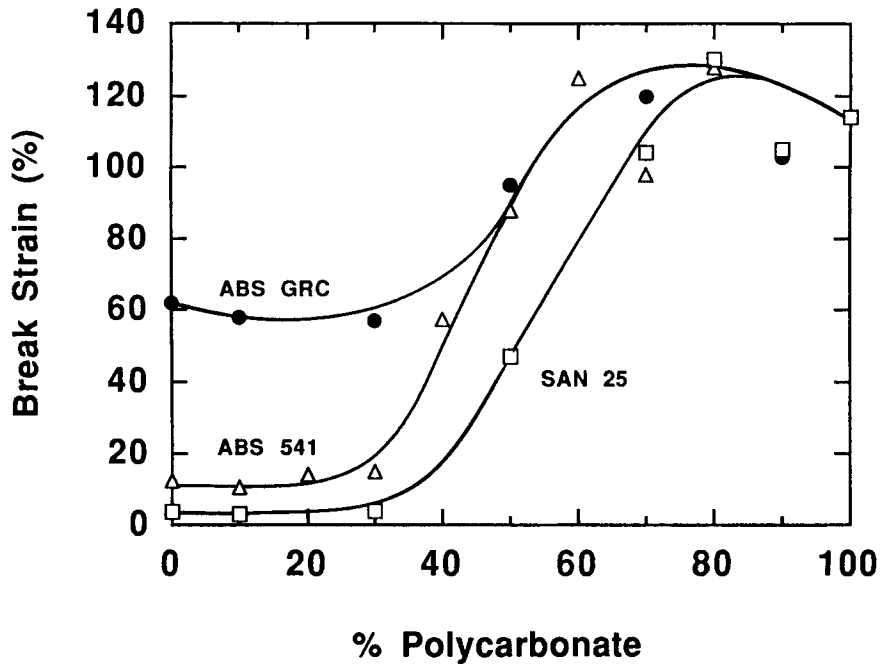


Figure 6 Break strain of PC blends with SAN 25, ABS 541, and ABS GRC.

exhibited an impact strength of 400 J/m. For compositions with more than 20% ABS 541, the data for sharp notches follow the same trend as for the

standard notch but at a slightly reduced impact strength level. PC-ABS GRC blends containing at least 5% ABS are very tough in sharp notch tests,

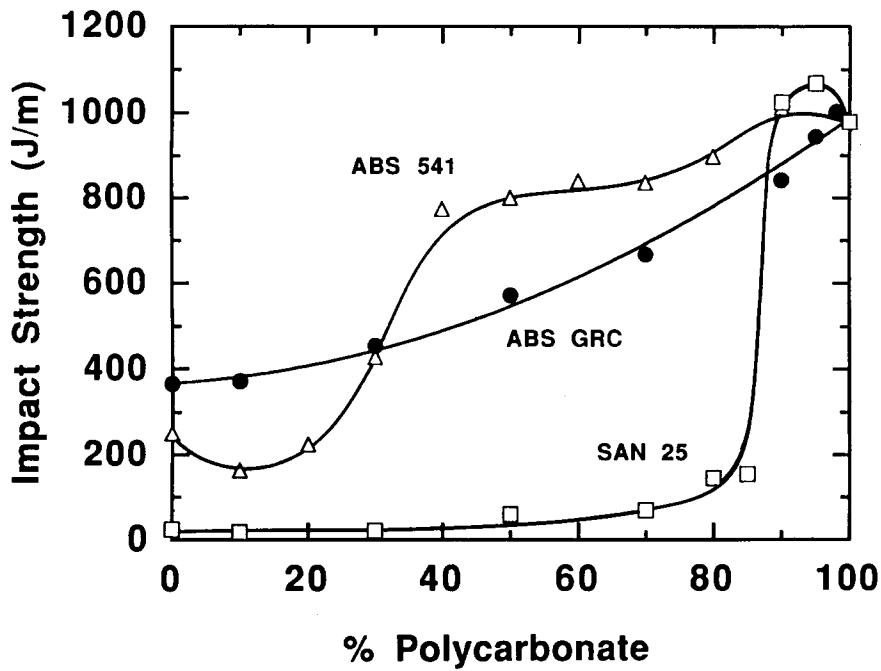


Figure 7 Standard notch Izod impact strength of PC blends with SAN 25, ABS 541, and ABS GRC.

falling just below the standard notch results. For blends with less than 5% ABS GRC, however, the sharp notch impact strength abruptly falls below 100 J/m. Similar results have been published by Cheng et al.⁵⁵

As the testing temperature is lowered, PC undergoes a transition from ductile to brittle behavior.

Increasing the PC molecular weight reduces the ductile to brittle transition temperature³⁵; the PC used here exhibits this transition at about -25°C . The ductile to brittle transition temperature of rigid polymers can be improved (lowered) by rubber modification. The extent of improvement is, in principle, limited ultimately by the T_g of the rubber

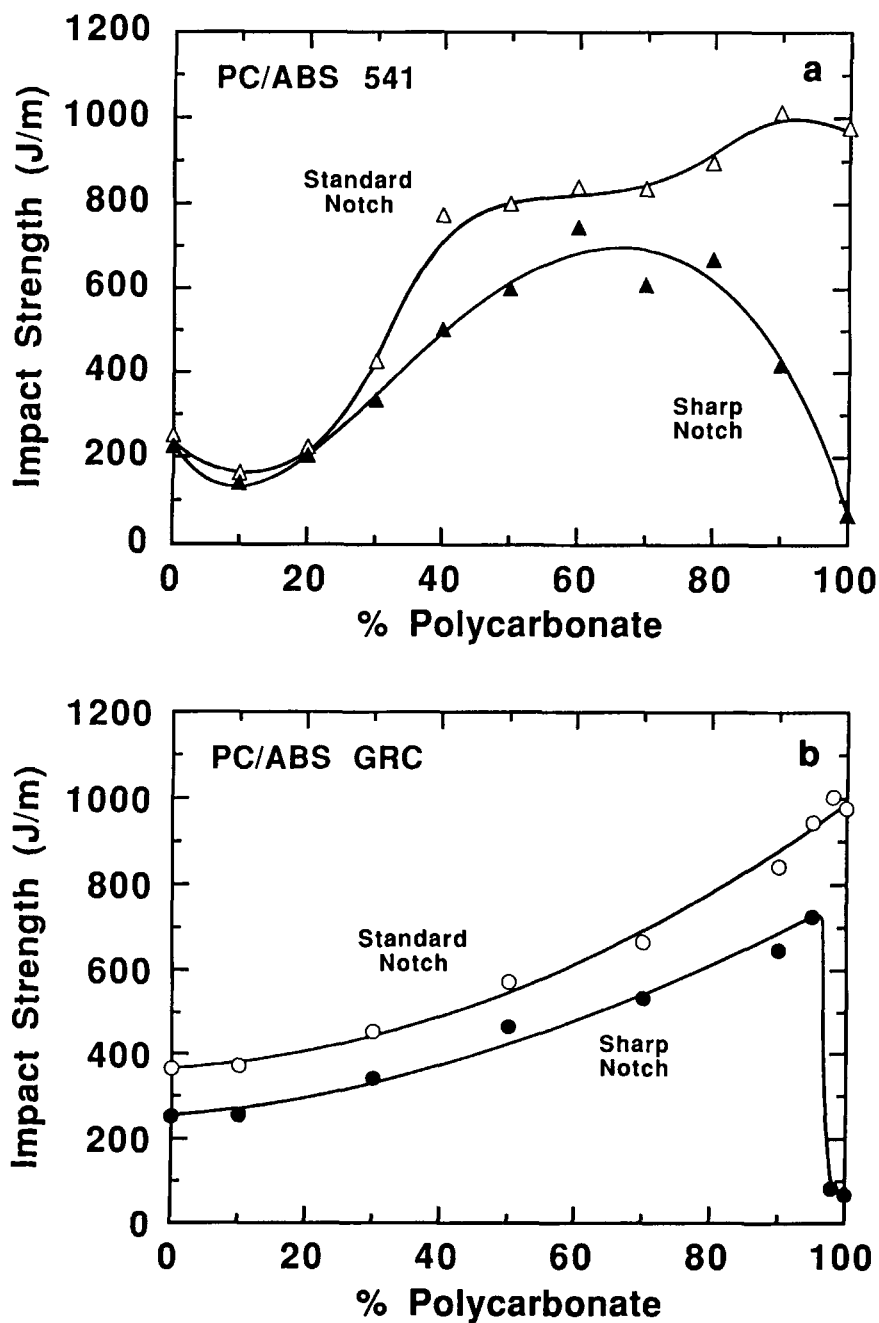


Figure 8 Standard notch and sharp notch Izod impact strength of PC blends with ABS 541 and ABS GRC.

modifier, although a number of factors can prevent reaching this extreme. The dynamic mechanical data in Figure 9 show that the T_g of the rubber in ABS 541 is -68°C and that the T_g of the rubber in ABS GRC is -55°C . The $\tan \delta$ peak in ABS 541 is sig-

nificantly smaller than that of ABS GRC because of the much lower rubber content of the former.

Figure 10 shows standard notch Izod impact strength data as a function of temperature for PC-ABS 541 and PC-ABS GRC blends containing 50,

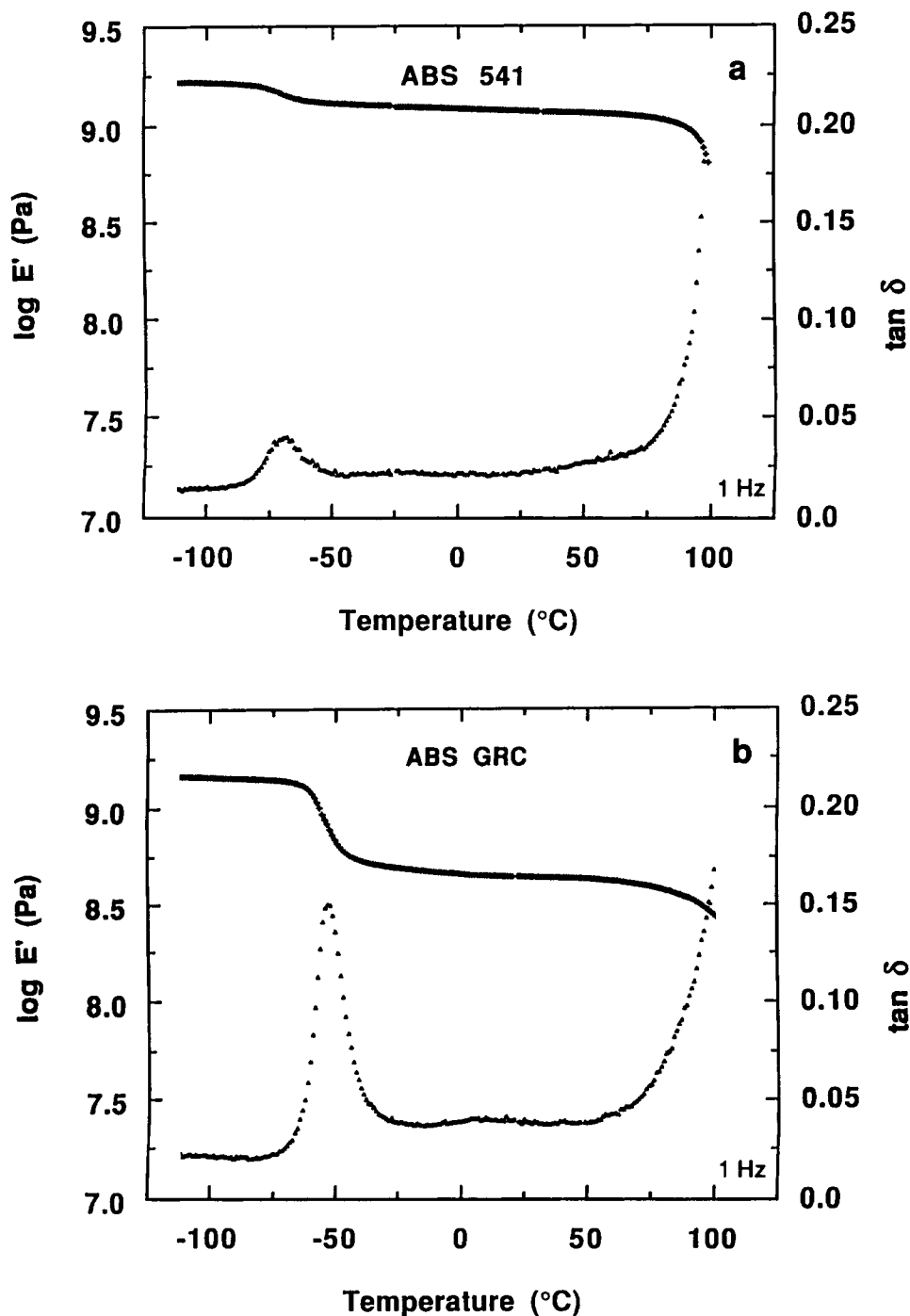


Figure 9 Dynamic mechanical thermal properties at 1 Hz of ABS 541 and ABS GRC.

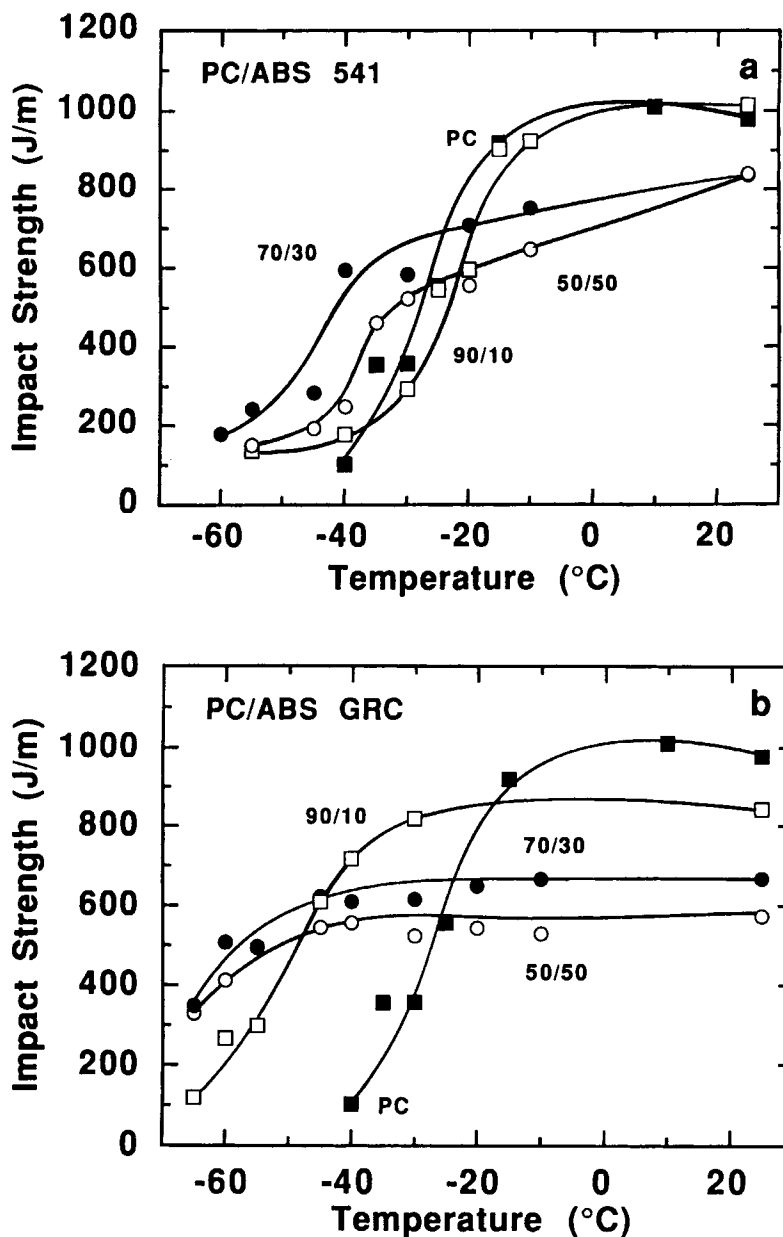


Figure 10 Low-temperature Izod impact strength (standard notch) for blends of PC blends with ABS 541 and ABS GRC.

70, and 90% PC. The ductile to brittle transition temperature is defined as the midpoint between the lowest temperature at which all specimens failed in a ductile manner and the highest temperature at which all specimens failed in a brittle manner. For the PC-ABS 541 blends, the 90/10 composition shows no improvement over the value of -25°C for PC, but the 50/50 blend becomes brittle at about -35°C , and the 70/30 blend becomes brittle at about -40°C . All three PC-ABS GRC blends show lower

ductile to brittle transition temperatures than the PC-ABS 541 blends. At 90% PC the transition is at about -50°C , and for the blends with 50 and 70% PC, the transition temperature as defined above appears to be about -60°C , which is 5°C below the reported T_g of the rubber (at 1 Hz) in ABS GRC. It should be noted that the PC-ABS GRC blends exhibit lower ductile to brittle transition temperatures than the PC-ABS 541 blends despite the higher T_g of the rubber in ABS GRC.

The results of this section indicate that the type of ABS material significantly affects the mechanical properties of PC-ABS blends. Rubber content clearly must be an important factor, but other variables including rubber particle size and morphology also must be considered.

EFFECT OF RUBBER PARTICLE TYPE IN ABS MATERIALS

Constant rubber concentration in ABS materials below 15% was achieved by blending ABS 541, ABS 611, or ABS GRC with SAN 25. Comparisons are

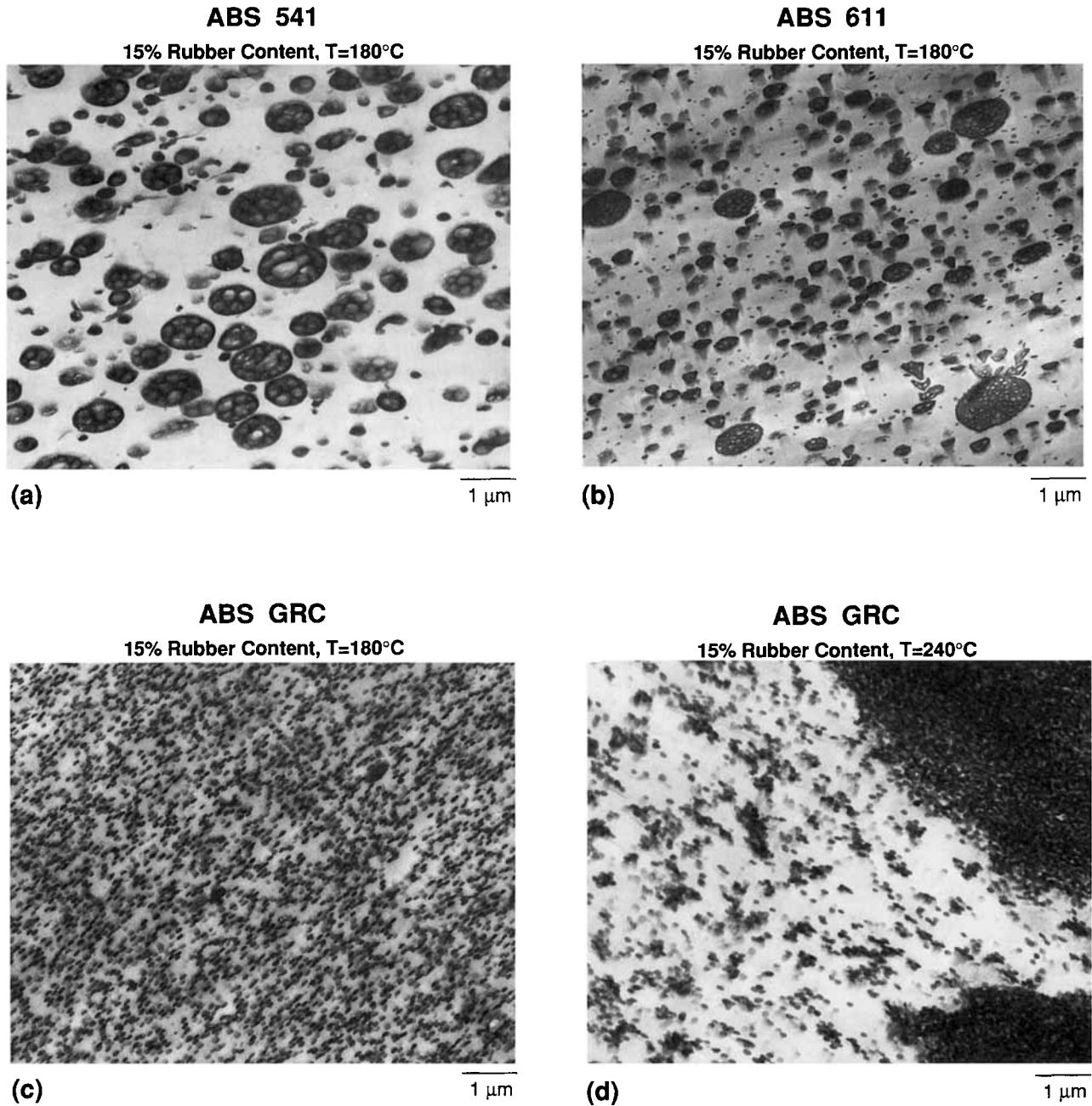


Figure 11 TEM photomicrographs of ABS materials made by blending ABS with SAN 25 to achieve a 15% rubber concentration. (a) ABS 541 at 180°C, (b) ABS 611 at 180°C, (c) ABS GRC at 180°C, and (d) ABS GRC at 240°C.

made at equal rubber concentrations regarding the effect of rubber particle type on the morphology and the mechanical properties of these materials.

Morphology

Figure 11 shows TEM photomicrographs of three different ABS materials containing 15% rubber. The different rubber particle types and sizes are evident from the photomicrographs. The rubber particles in these materials remain well dispersed during melt blending with SAN 25 at 180°C, but the rubber particles in ABS GRC are agglomerated at higher processing temperatures. Figure 12(d) shows the agglomerated rubber particles in ABS GRC after extrusion blending at 240°C.

Rubber Particle Agglomeration

Aoki⁶⁴ reported that a low degree of grafting could cause rubber particles to agglomerate in ABS. He also discussed that there is a critical grafting degree required to prevent agglomeration and that this value will change with particle size. At a constant degree of grafting, the effective covering of the rubber particle by the grafted SAN decreases as the particle size decreases. Rough calculations and experimental results support the speculation that agglomeration in ABS GRC is caused by a low degree of grafting.⁶²

Although it is possible to produce a material like ABS GRC with rubber particles that do not agglomerate, one was not available for this study. In practice, aggregated rubber particles can provide a technological advantage. For example, several patents discuss rubber particle aggregation and grafting degree in relation to the mechanical properties and the aesthetic qualities of ABS materials and PC-ABS blends.^{3,8,11}

Mechanical Properties

Table II shows that mixtures of SAN 25 with ABS 541 and ABS 611 are tough at rubber concentrations greater than 10%. However, mixtures with ABS GRC are not tough at rubber concentrations at or below 15% where the rubber particles are well dispersed. When the rubber particles are agglomerated, these mixtures exhibit improved impact strength at 15% rubber content. These results suggest that the presence of some larger rubber particles is beneficial in enhancing the toughness of ABS. At 10 and 15% rubber content, mixtures of SAN 25 with both ABS 541 and ABS 611 exhibit similar impact strengths, indicating that a combination of small and large particles is effective for toughening.

The data in Table II show that rubber particle type does not affect the modulus or tensile strength of the ABS materials, but the break strain seems to be consistently lower for the well-dispersed ABS GRC particles. The break strain data follow the trends of the impact strength results.

Table II Mechanical Properties of ABS Materials Containing Different Rubber Concentrations

Base ABS material	Rubber Content (wt %)	Processing Temperature (°C)	Izod Impact Strength (J m ⁻¹), Standard Notch	Modulus (GPa)	Tensile Strength (MPa)	Break Strain (%)
No ABS (100% SAN 25)	0	180	24	3.54	70	3.7
ABS 541	5	180	51	3.16	67	7.0
ABS 611	5	180	19	2.98	70	6.1
ABS GRC	5	180	20	2.98	65	6.2
ABS GRC	5	240	26	3.00	61	5.1
ABS 541	10	180	175	2.65	57	9.1
ABS 611	10	180	150	2.47	60	8.8
ABS GRC	10	180	30	2.65	55	7.4
ABS GRC	10	240	44	2.64	51	10.1
ABS 541	15	180	310	2.25	47	9.3
ABS 611	15	180	317	2.23	54	11.0
ABS GRC	15	180	33	2.32	47	7.3
ABS GRC	15	240	82	2.23	42	16.3

EFFECT OF RUBBER PARTICLE TYPE IN PC-ABS BLENDS

The effect of rubber particle type on the morphology and the mechanical properties of PC-ABS blends at three different blend compositions (50/50, 70/30, and 90/10) are considered. The ABS materials having constant rubber concentrations discussed in the preceding section were used to prepare PC-ABS blends. At each PC-ABS ratio, the morphology and

the mechanical properties of the blends are explored as a function of rubber concentration in the ABS phase. The effect of rubber particle type is separated from the effect of rubber content by making comparisons at equal rubber concentrations.

50/50 Blends

Figure 12 shows TEM photomicrographs of 50/50 blends of polycarbonate with ABS materials con-

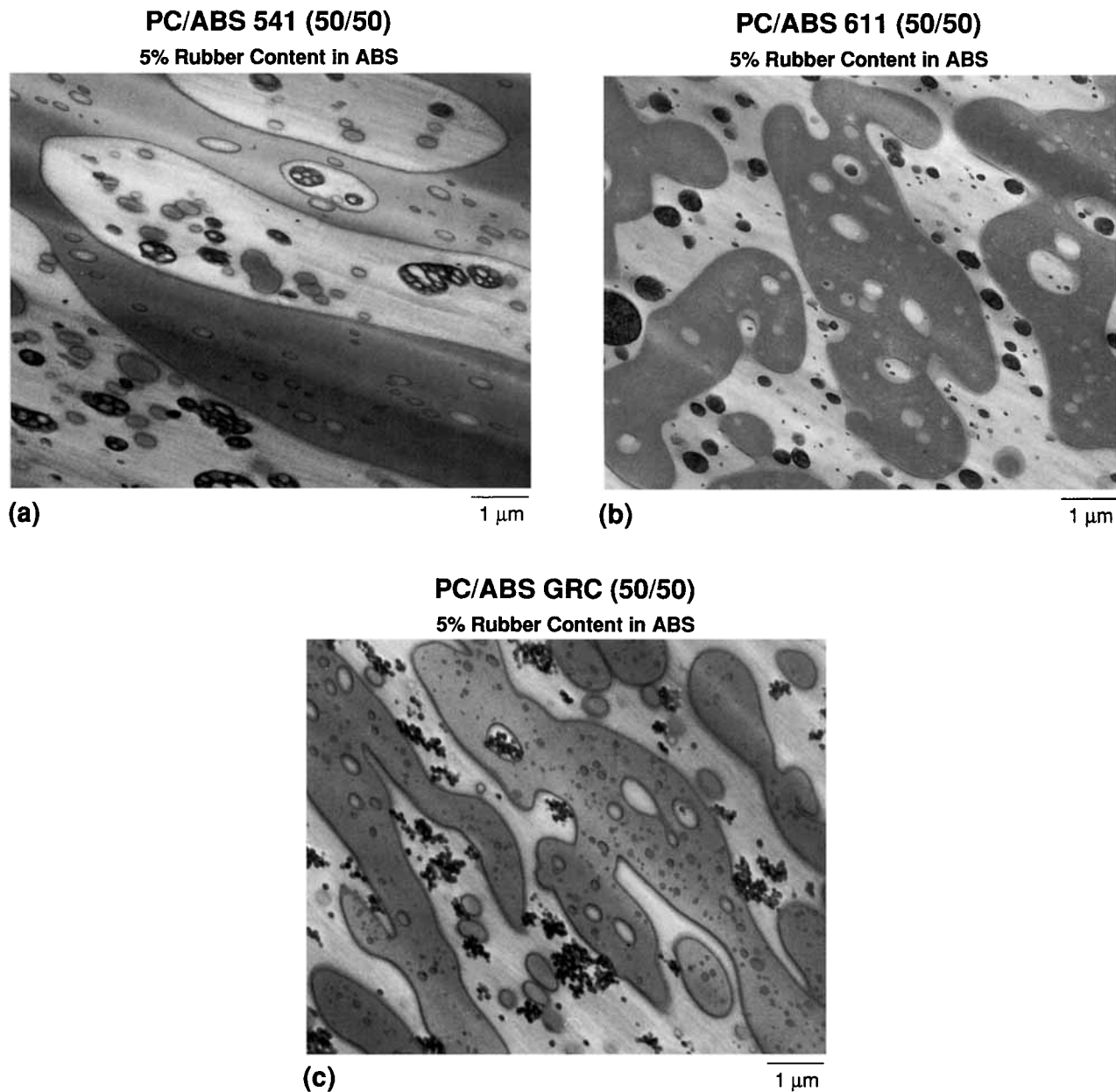


Figure 12 TEM photomicrographs of 50/50 blends of PC with ABS materials containing 5% rubber. (a) PC-ABS 541, (b) PC-ABS 611, (c) PC-ABS GRC.

taining 5% rubber. In all three blends, PC and ABS phases form a complex co-continuous morphology. The SAN phase contains isolated PC domains, and the PC phase contains many small SAN occlusions. The principal PC and SAN phases in the ABS-541-based blend appear larger than those in the ABS-611-based and ABS-GRC-based blends. In the ABS-541-based and the ABS-611-based blends, the rubber particles are well dispersed throughout the principal SAN phase. In the ABS-GRC-based blend, however, the rubber particles form small aggregates that are evenly dispersed throughout the principal SAN phase. All three PC-ABS blends have individual rubber particles located within some of the occluded SAN domains. The ABS-611-based blend shows more rubber particles within the occluded SAN domains than the other PC-ABS blends show, and the ABS-GRC-based mixture contains both agglomerated particles and individual particles within some occluded SAN domains.

Table III lists the tensile properties of the PC-ABS blends. The tensile modulus and the tensile strength increase with decreasing rubber content, but no significant differences are observed between blends at equal rubber concentrations. Strain at break appears to decrease as the rubber content in the ABS is reduced. All of the PC-ABS blends with 5% rubber in ABS showed considerable scatter. In PC-SAN 25 blends, the break strains range from 30 to 60%. The values of break strain for the ABS-541-based blends are consistently lower than those for blends using the other two ABS materials. Some specimens of ABS-541-based blends broke at about 25% elongation, but some broke above 100%. In the

PC-ABS (50/50) blends, the type of rubber particle does not significantly affect the blend modulus or tensile strength, but it does appear to influence the strain at break.

Figure 13 shows the Izod impact strength of PC blends with different ABS materials at room temperature. At 15% rubber content in the ABS, the standard notch impact strength is around 800–1000 J/m, and the sharp notch impact strength is about 600–800 J/m. As rubber content is decreased, blend ductility is reduced, but these materials remain exceptionally tough at rubber concentrations above 8% in ABS. The standard notch data show that the ABS-611-based and the ABS-GRC-based blends are consistently 200 J/m tougher than the ABS-541-based blends in the transition region between 5 to 10% rubber content. The sharp notch data show similar trends.

Figure 14 shows the standard notch Izod impact strength for PC-ABS (50/50) blends at three different rubber levels as a function of temperature. The blends based on ABS materials containing 5% rubber drop to below 200 J/m at 0°C. The blends with 10% rubber differ in low-temperature impact strength depending on the ABS type. The ABS-GRC-based blends remain significantly tougher than the ABS-based and the ABS-541-based blends between 0 and –15°C, but none exhibit ductile to brittle transitions as low as the high molecular weight PC. For blends with 15% rubber in the ABS component, the ABS-GRC-based blend is significantly tougher at low temperatures between –20 and –35°C. The ABS-GRC-based blend exhibits a ductile to brittle transition temperature lower than PC (–25°C), but the ABS-541-based blend and the

Table III 50/50 Blends of PC with ABS Materials Containing Different Rubber Particle Types and Concentrations

50/50 Blend of PC with ABS Based on	Rubber Content of ABS (wt %)	Modulus (GPa)	Tensile Strength (MPa)	Break Strain (%)
No ABS (100% SAN 25)	0	2.77	73	47
ABS 541	5	2.62	65	83
ABS 611	5	2.60	64	71
ABS GRC	5	2.59	63	72
ABS 541	10	2.39	58	56
ABS 611	10	2.46	62	109
ABS GRC	10	2.42	56	112
ABS 541	15	2.18	54	89
ABS 611	15	2.26	59	120
ABS GRC	15	2.18	51	119

ABS-611-based blend are less tough at this temperature. However, blends based on ABS 541 are tougher in the -20 to -30°C temperature range than those based on ABS 611.

70/30 Blends

Figure 15 shows TEM photomicrographs of 70/30 blends of polycarbonate with ABS materials con-

taining 5% rubber. Polycarbonate forms the continuous phase in all three blends at this composition. In the ABS-541-based blend, the SAN component forms two distinct domain size populations: small spherical domains ($0.1-1\ \mu\text{m}$) and large irregular domains ($1-10\ \mu\text{m}$). Most of the rubber particles are contained within the large SAN domains. In the ABS-611-based and the ABS-GRC-based blends, most of the SAN domains are spherical, with a broad

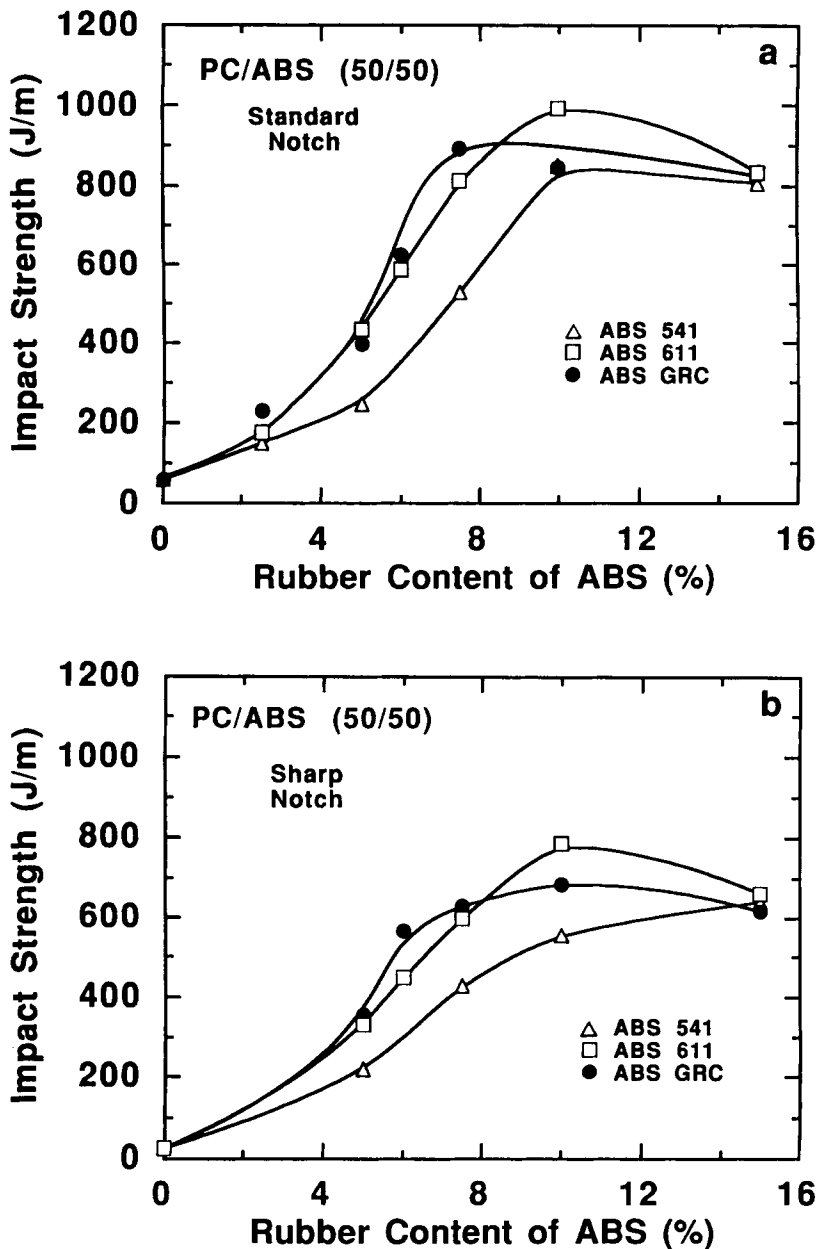


Figure 13 Izod impact strength as a function of rubber concentration in ABS for 50/50 blends of PC with ABS 541, ABS 611, and ABS GRC.

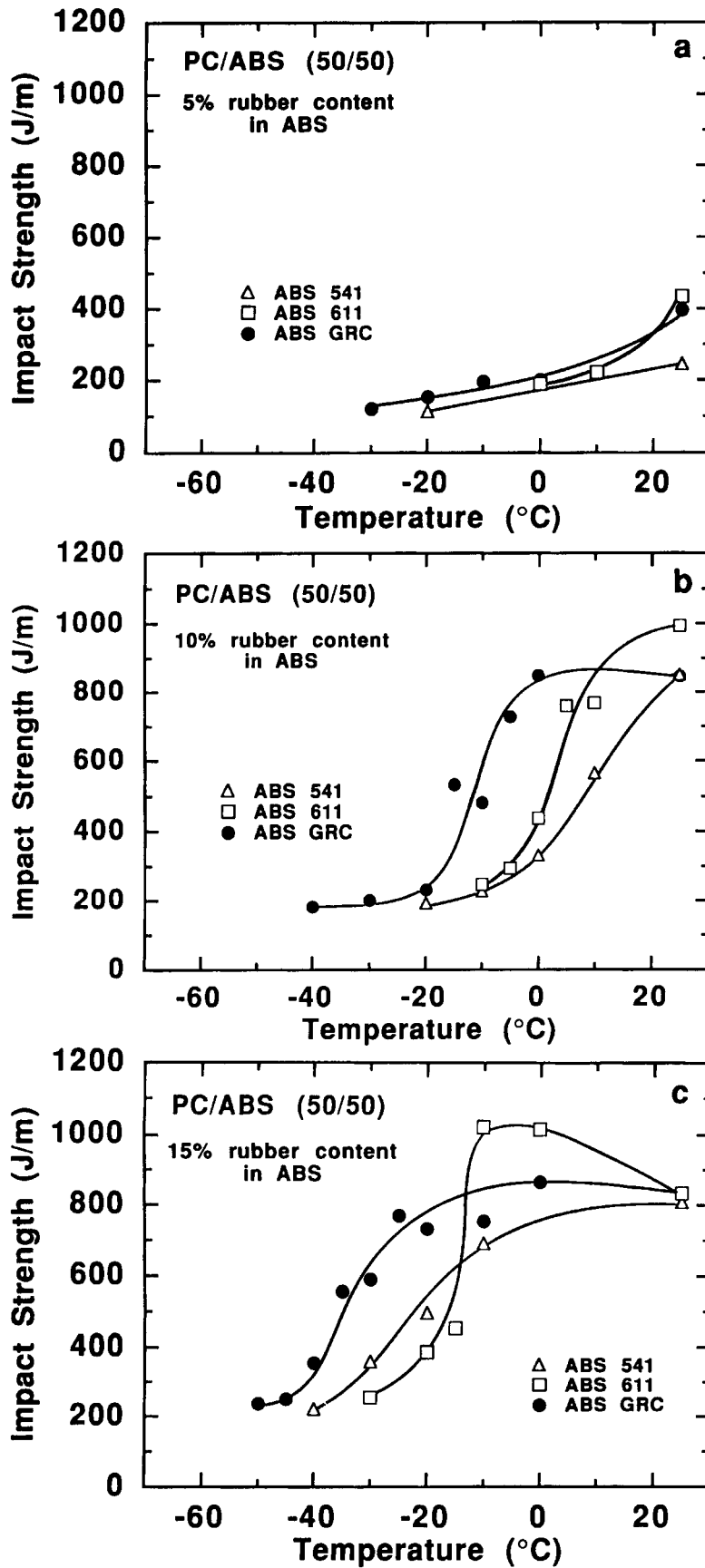


Figure 14 Low-temperature Izod impact strength (standard notch) at 5, 10, and 15% rubber concentration in ABS for 50/50 blends of PC with ABS 541, ABS 611, and ABS GRC.

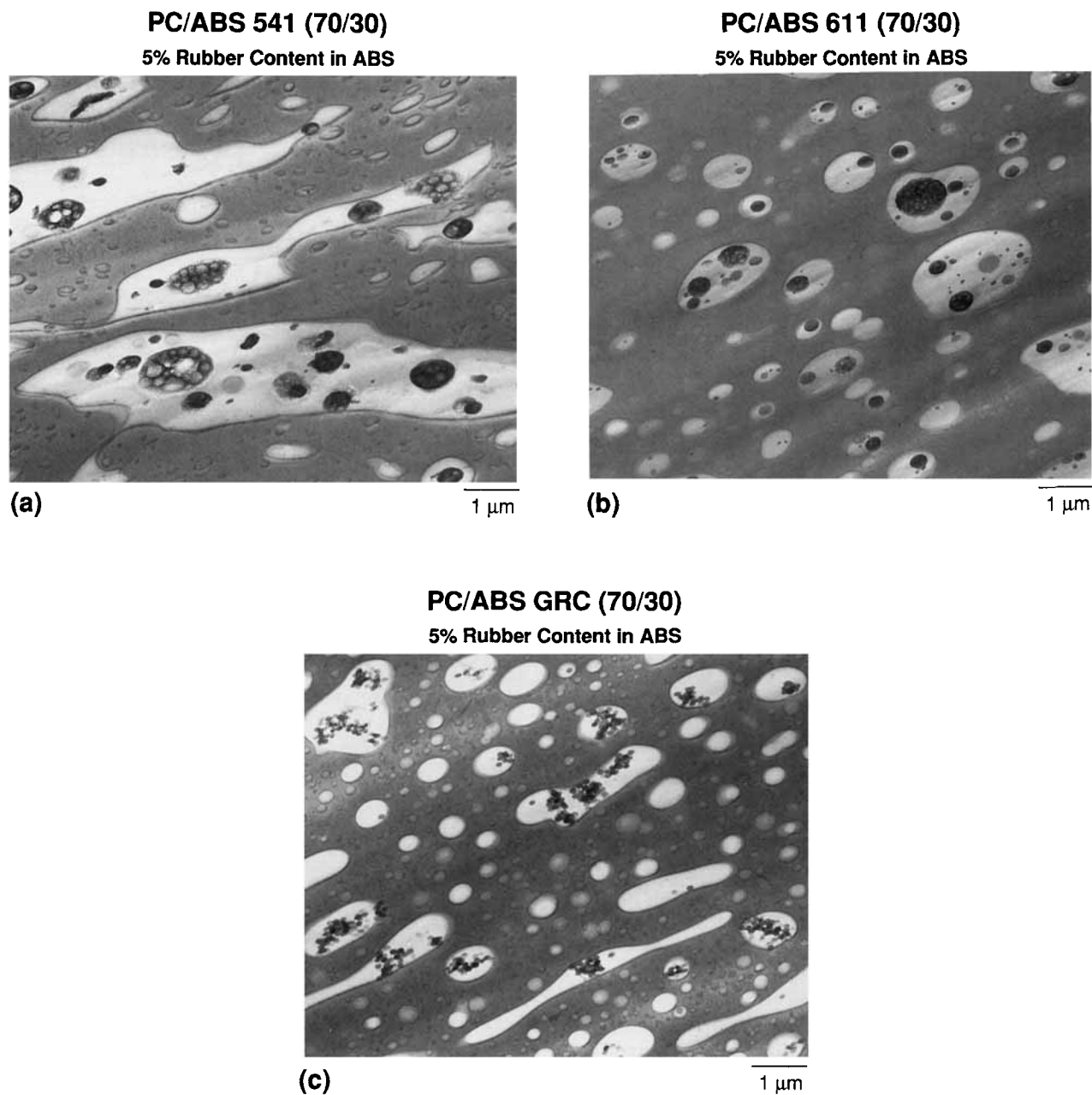


Figure 15 TEM photomicrographs of 70/30 blends of PC with ABS materials containing 5% rubber. (a) PC-ABS 541, (b) PC-ABS 611, (c) PC-ABS GRC.

size distribution (0.1–2 μm), but some are elongated. In the ABS-611-based blend, the rubber particles are well dispersed and evenly distributed among the SAN domains. In the ABS-GRC-based blend, both aggregates of rubber particles and a few individual particles are observed within the SAN, but they do not appear to be as well distributed as the rubber particles in the ABS-611-based blend with PC.

Table IV shows the tensile properties of PC blends with different ABS materials at the 70/30 composition. The tensile modulus and the tensile strength increase with decreasing rubber content, but no significant differences are observed between blends at equal rubber concentrations. The ABS-541-based blends at 5 and 10% rubber content in the ABS show slightly higher modulus values, but

Table IV 70/30 Blends of PC with ABS Materials Containing Different Rubber Particle Types and Concentrations

70/30 Blend of PC with ABS Based on	Rubber Content of ABS (wt %)	Modulus (GPa)	Tensile Strength (MPa)	Break Strain (%)
No ABS (100% SAN 25)	0	2.48	67	105
ABS 541	5	2.46	65	100
ABS 611	5	2.38	64	125
ABS GRC	5	2.34	63	116
ABS 541	10	2.44	61	116
ABS 611	10	2.30	62	112
ABS GRC	10	2.19	59	115
ABS 541	15	2.16	58	100
ABS 611	15	2.21	59	120
ABS GRC	15	2.09	55	117

these are not significantly different from values for blends using the other ABS materials. The variability most likely is a result of orientation differences in the injection-molded test specimens. All of the blends at this composition exhibited break strains in excess of 100%. The strain at break for these blends were not affected by the changing rubber concentration or rubber particle type.

Figure 16 shows the Izod impact strength of PC blends with different ABS materials at the 70/30 composition. At 15% rubber content in the ABS, the standard notch impact strength is approximately 850 J/m, and the sharp notch impact strength is about 550 J/m. As the rubber content in the ABS is decreased to 5%, the blends remain tough at 800 J/m and 400 J/m for standard notch and sharp notch, respectively. As the rubber content is decreased further, the blends become brittle. However, at about 3.5% rubber in ABS, the blends remain exceptionally tough. The ductile to brittle transitions are sharper for the 70/30 blends than for the 50/50 blends. For the standard notch impact data, the transition for ABS-541-based blends occurs at about 3% rubber content, but the transition occurs at approximately 1.5% for the blends based on ABS 611. For ABS-GRC-based materials, the transition is at 2.5% rubber content. Again the same general trends are observed in the sharp notch data, although the blends become brittle at slightly higher rubber contents.

Figure 17 shows low temperature Izod impact results for PC-ABS (70/30) blends at three different rubber contents. For this composition, the effect of ABS or rubber particle types is not great. The ductile

to brittle transition temperature is 5°C at 5% rubber, -25°C at 10% rubber, and -35°C at 15% rubber.

A series of experiments, comparable to those in sections on 50/50 and 70/30 blends, was carried out on blends of 90/10 PC-ABS ratios.⁶² The results indicated that no significant benefits accrued with these blends, particularly because the critical properties of sharp notch Izod impact strength and ductile to brittle transition temperature were not sufficiently improved in comparison to PC.

SUMMARY

The effects of different ABS materials on the morphology and the mechanical properties of PC-ABS blends are reported. In the first section important differences are shown between PC-ABS blends containing a mass-made ABS with 16% rubber content and large particles (0.5–1 μm) and those containing an emulsion-made ABS with 50% rubber content and small particles (0.12 μm). The blends made with the emulsion-produced ABS show lower modulus and tensile strength, but they exhibit excellent toughness in standard and sharp notch Izod impact tests at room temperature and in standard notch Izod impact tests at low temperatures near the T_g of the rubber. These results can be attributed in part to the high rubber content of the ABS, but rubber particle size, composition, and distribution also might play a role.

The effect of rubber particle type was separated from the effect of rubber content by comparing properties of blends with PC based on different ABS

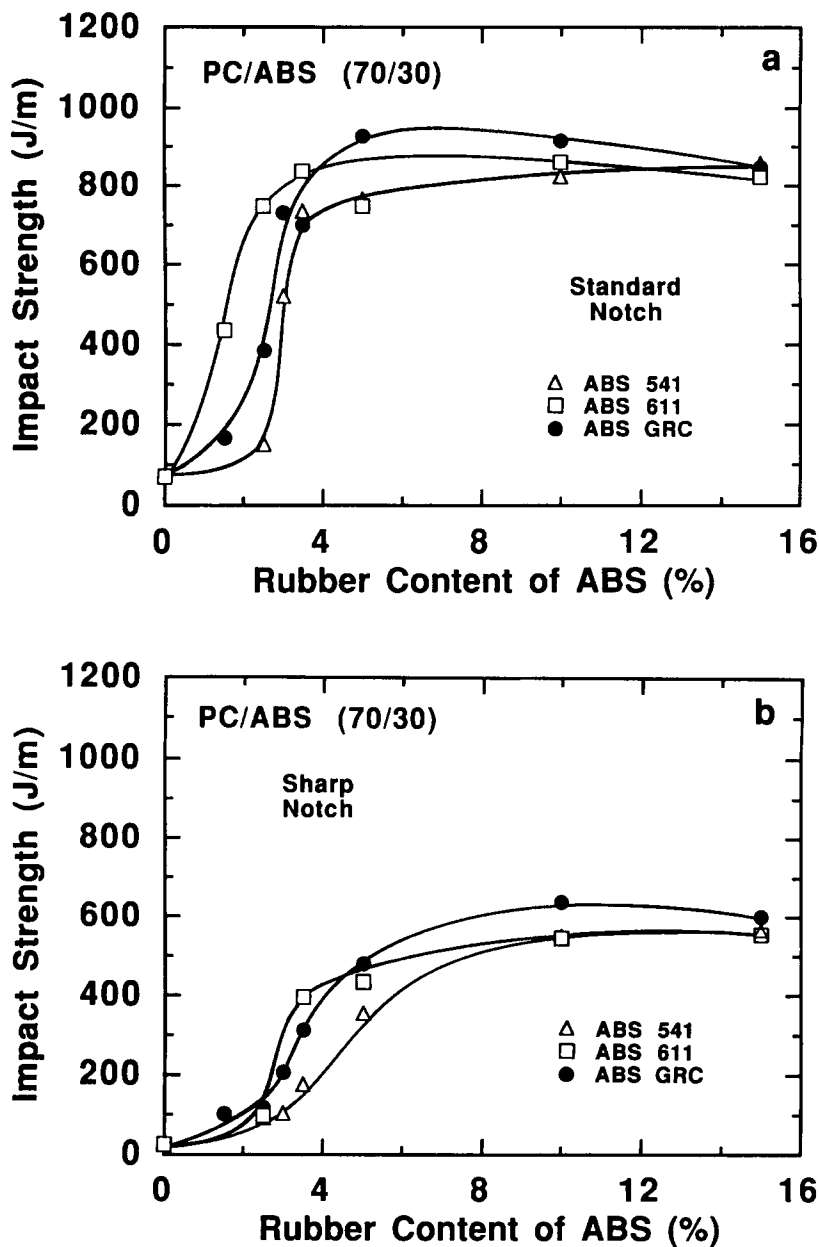


Figure 16 Izod impact strength as a function of rubber concentration in ABS for 70/30 blends of PC with ABS 541, ABS 611, and ABS GRC.

materials at equal rubber concentrations in the ABS phase. The results of this investigation show that brittle ABS materials can produce tough PC-ABS blends at compositions where PC-SAN 25 blends are brittle. It is also concluded that small rubber particles toughen PC-ABS blends at lower rubber concentrations and at lower temperatures than is possible with large rubber particles. Interestingly, ABS-GRC-based blends are consistently tougher

than ABS-541-based blends at equal rubber concentrations despite the T_g of the rubber in ABS 541 being more than 10°C less than the T_g of the rubber in ABS GRC.

In general, the blends based on ABS GRC have better low-temperature impact properties. ABS-GRC-based materials are primarily distinguished by the small, uniform emulsion particles. However, it is somewhat speculative to attribute all these effects

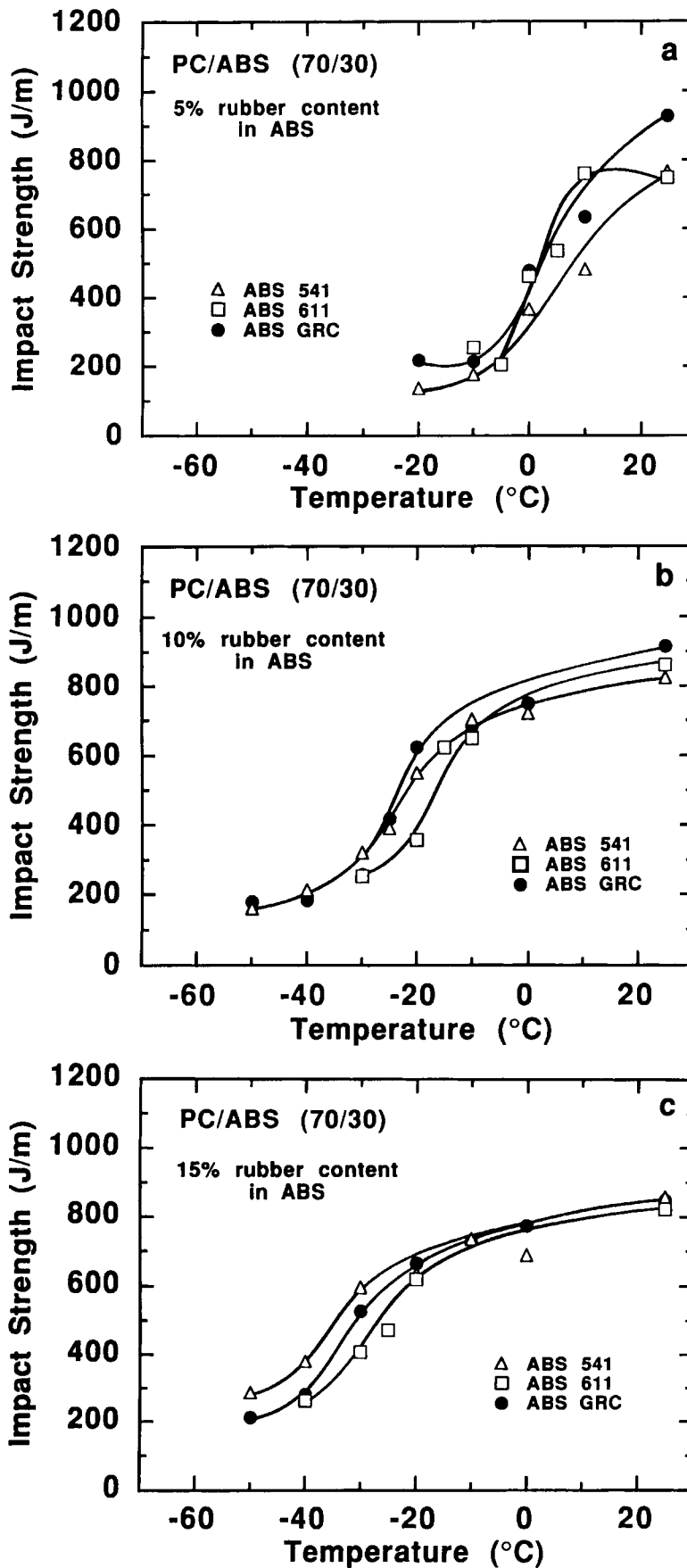


Figure 17 Low-temperature Izod impact strength (standard notch) at 5, 10, and 15% rubber in ABS for 70/30 blends of PC with ABS 541, ABS 611, and ABS GRC.

to that single reason because other factors associated with morphology, component molecular weight, grafting degree, etc., might be involved as well. Also, it is important to note that the true effects of the small GRC rubber particle size are masked to some extent by the agglomeration of these particles.

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REFERENCES

1. T. S. Grabowski, U.S. Pat. 3,130,177 (April 21, 1964) (to Borg-Warner Corp.).
2. H. S. Chao, U.S. Pat. 5,229,169 (July 20, 1993) (to General Electric Co.).
3. D. L. Dufour and J. P. St. Denis, U.S. Pat. 5,061,754 (October 29, 1991) (to Monsanto Europe S.A.).
4. R. Dujardin, J. Schoeps, and M. Wandel, U.S. Pat. 5,177,145 (January 5, 1993) (to Bayer A.G.).
5. T. Eckel, D. Wittmann, D. Freitag, U. Westeppe, and K. H. Ott, U.S. Pat. 5,137,970 (August 11, 1992) (to Bayer A.G.).
6. J. D. Fischer, R. B. Darmstadt, U. Numrich, and W. Siol, U.S. Pat. 5,232,986 (August 3, 1993) (to Rohm GmbH Chemische Fabrik).
7. S. K. Gaggar, U.S. Pat. 5,128,409 (July 7, 1992) (to General Electric Co.).
8. D. E. Henton and T. O'Brien, U.S. Pat. 4,419,496 (December 6, 1983) (to Dow Chemical Co.).
9. H. C. Kao, M. M. Lee, C. C. Chiang, J. L. Lin, and T. K. Wu, U.S. Pat. 5,055,505 (October 8, 1991) (to Industrial Technology Research Institute).
10. R. Neumann, B. Ehrenfried, K. Benker, and K. Ruppnich, U.S. Pat. 5,162,423 (November 10, 1992) (to BASF A.G.).
11. C. M. M. Pottier-Metz and M. Erpelding, U.S. Pat. 5,162,419 (November 10, 1992) (to GE Plastics ABS Europe B.V.).
12. H. L. Rawlings and G. E. Reinert, U.S. Pat. 4,487,881 (July 30, 1991) (to Mobay Chemical Corp.).
13. M. K. Rinehart and J. J. Ziegelmeyer, U.S. Pat. 5,036,126 (July 30, 1991) (to General Electric Co.).
14. K. Udipi, U.S. Pat. 5,082,897 (January 21, 1992) (to Monsanto Co.).
15. K. Udipi, U.S. Pat. 5,104,934 (April 14, 1992) (to Monsanto Co.).
16. D. R. Paul, J. W. Barlow, and H. Keskkula, in *Encyclopedia of Polymer Science and Engineering*, 2nd ed., H. F. Mark, N. H. Bikales, C. G. Overberger, and G. Menges, Eds., Wiley, New York, Vol. 12, 1988, p. 399.
17. W. Y. Chiang and D. S. Hwung, *Polym. Eng. Sci.*, **27**, 632 (1987).
18. W. K. Chin and J. L. Hwang, *SPE ANTEC Tech. Papers*, **45**, 1379 (1987).
19. J. H. Chun, K. S. Maeng, and K. S. Suh, *J. Mater. Sci.*, **26**, 5347 (1991).
20. L. Dong, R. Greco, and G. Orsello, *Polymer*, **34**, 1375 (1993).
21. R. Greco, M. F. Astarita, and L. Dong, to appear.
22. R. Greco, M. F. Astarita, and L. Dong, to appear.
23. J. J. Herpels and L. Mascia, *Eur. Polym. J.*, **26**, 997 (1990).
24. M. Ishikawa and I. Chiba, *Polymer*, **31**, 1232 (1990).
25. M. S. Lee, H. C. Kao, C. C. Chiang, and D. T. Su, *Adv. Polym. Blends Alloys Tech.*, **2**, 25 (1989).
26. M. P. Lee, Ph.D. Thesis, Case Western Reserve University, 1991.
27. M. P. Lee, A. Hiltner, and E. Baer, *Polymer*, **33**, 685 (1992).
28. M. P. Lee, A. Hiltner, and E. Baer, *Polym. Eng. Sci.*, **32**, 909 (1992).
29. L. Morbitzer, H. J. Krebs, C. Lindner, and K. H. Ott, *Angew. Makromol. Chem.*, **132**, 19 (1985).
30. S. V. Nair, L. Vestergaard, M. L. Shiao, L. A. Goettler, and W. D. Henry, *SPE ANTEC Tech. Papers*, **51**, 3279 (1993).
31. S. Seidler and W. Grellmann, *J. Mater. Sci.*, **28**, 4078 (1993).
32. D. Stefan and H. L. Williams, *J. Appl. Polym. Sci.*, **18**, 1451 (1974).
33. H. Suarez, J. W. Barlow, and D. R. Paul, *J. Appl. Polym. Sci.*, **29**, 3253 (1984).
34. G. Weber and J. Schoeps, *Angew. Makromol. Chem.*, **136**, 45 (1985).
35. J. S. Wu, S. C. Shen, and F. C. Chang, *J. Appl. Polym. Sci.*, **50**, 1379 (1993).
36. W. N. Kim and C. M. Burns, *Polym. Eng. Sci.*, **28**, 1115 (1988).
37. T. Kurauchi and T. Ohta, *J. Mater. Sci.*, **19**, 1699 (1984).
38. R. A. Mendelson, *J. Polym. Sci. Polym. Phys. Ed.*, **23**, 1975 (1985).
39. L. L. Berger and E. J. Kramer, *J. Mater. Sci.*, **22**, 2739 (1987).
40. T. A. Callaghan, K. Takakuwa, D. R. Paul, and A. R. Padwa, *Polymer*, **34**, 3796 (1993).
41. B. L. Gregory, A. Siegmann, J. Im, A. Hiltner, and E. Baer, *J. Mater. Sci.*, **22**, 532 (1987).
42. B. Gregory, A. Hiltner, and E. Baer, *Polym. Eng. Sci.*, **27**, 568 (1987).
43. M. J. Guest and J. H. Daly, *Eur. Polym. J.*, **25**, 985 (1989).
44. M. J. Guest and J. H. Daly, *Eur. Polym. J.*, **26**, 603 (1990).
45. V. Janarthanan, R. S. Stein, and P. D. Garrett, *J. Polym. Sci. Polym. Phys. Ed.*, **31**, 1995 (1993).
46. J. D. Keitz, J. W. Barlow, and D. R. Paul, *J. Appl. Polym. Sci.*, **29**, 3131 (1984).

47. M. Kodama, *Polym. Eng. Sci.*, **33**, 1141 (1993).
48. K. K. Koo, T. Inoue, and K. Miyasaka, *Polym. Eng. Sci.*, **25**, 741 (1985).
49. M. Ma, A. Hiltner, E. Baer, and J. Im, *SPE ANTEC Tech. Papers*, **46**, 1525 (1988).
50. D. Quintens, G. Groeninckx, M. Guest, and L. Aerts, *Polym. Eng. Sci.*, **30**, 1484 (1990).
51. D. Quintens, G. Groeninckx, M. Guest, and L. Aerts, *Polym. Eng. Sci.*, **30**, 1474 (1990).
52. R. E. Skochdopole, C. R. Finch, and J. Marshall, *Polym. Eng. Sci.*, **27**, 627 (1987).
53. F. C. Chang, J. S. Wu, and L. H. Chu, *J. Appl. Polym. Sci.*, **44**, 491 (1992).
54. T. W. Cheng, H. Keskkula, and D. R. Paul, *J. Appl. Polym. Sci.*, **45**, 1245 (1992).
55. T. W. Cheng, H. Keskkula, and D. R. Paul, *J. Appl. Polym. Sci.*, **45**, 531 (1992).
56. T. W. Cheng, H. Keskkula, and D. R. Paul, *Polymer*, **33**, 1606 (1992).
57. D. Debier, J. Devaux, R. Legras, and D. LeBlanc, to appear.
58. D. S. Parker, H. J. Sue, J. Huang, and A. F. Yee, *Polymer*, **31**, 2267 (1990).
59. D. W. Gilmore and M. J. Modic, *Plastics Engineering*, **45**, 51 (1989).
60. H. Kim, H. Keskkula, and D. R. Paul, *Polymer*, **31**, 869 (1990).
61. G. E. Molau, *Polym. Lett.*, **3**, 1007 (1965).
62. B. S. Lombardo, M.S. Thesis, The University of Texas at Austin, 1994.
63. B. Mujundar, Ph.D. Thesis, The University of Texas at Austin, 1994.
64. Y. Aoki, *Macromolecules*, **20**, 2208 (1987).

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