

Mechanical Properties of Polycarbonate/Modified Acrylonitrile-Styrene-Acrylate Terpolymer Blend

Amol A. Ramteke,¹ S. N. Maiti²

¹Department of Polymer Technology, College of Engineering and Technology, Akola 444104, India

²Centre for Polymer Science and Engineering, Indian Institute of Technology, New Delhi 110016, India

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ABSTRACT: Modified acrylonitrile-styrene-acrylate (MASA) were prepared by grafting with maleic anhydride and optimization was carried out. The compatibilizer with four parts of ASA-g-MA in 10 parts of acrylonitrile-styrene-acrylate (ASA) was found effective in improving the interface. On that basis, the different compositions of blends of polycarbonate (PC)/MASA terpolymer were compounded using a twin screw extruder. The blends granules were then injection molded into a standard tensile specimens for mechanical, dynamic mechanical, and morphology characterization. The mechanical properties, such as, tensile behavior of melt mixed PC/modified ASA terpolymer blends at MASA content up to 52 vol % were evaluated. The tensile strength decreased with MASA con-

centration has been analyzed on the basis of interphase adhesion. Impact strength and elongation were increased with increase in ASA concentration up to 10 phr. Tensile modulus shows decrease with addition of ASA. Predictive models have been used to explain the tensile strength and modulus properties. The tensile modulus shows slightly negative deviation from rule of mixture indicating reduction in stiffness. Dynamic mechanical analysis shows evidence of partial miscibility. Morphology observations were also carried out to further insight into the system. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 486–492, 2010

Key words: PC/MASA blends; interphase adhesion; stress concentration; ASA-g-MA

INTRODUCTION

Polycarbonate (PC) is an engineering thermoplastic material with excellent combination of properties. The notch sensitive behavior of PC can be reduced by blending with ABS, a terpolymer. The styrene-based terpolymers were originally used to the extent of some 2–9% in order to reduce the notch sensitivity of PC.¹ Several researchers have been investigating the mechanical performance of PC/ABS blends. In general, the morphology and the mechanical properties of PC/ABS blends depend on PC molecular weight, processing conditions and type, size, and content of ABS rubber.^{2–7}

It has been reported in the literature that PC is partially miscible in ABS due to favorable thermodynamic interaction between PC and styrene-acrylonitrile (SAN) copolymer matrix of ABS, but the extent of partial miscibility is very limited and should produce small shift in the glass transition temperature.⁸ However, some workers reported that the shift in the glass transition temperature can be attributed to the low molecular weight SAN species migration

toward PC boundary domains during melt mixing rather than partial miscibility.^{9,10} Reactive compatibilization via melting grafting with maleic anhydride (MA) of ABS has been studied by several researchers.^{11–15} PC can also effectively blend with acrylonitrile-styrene-acrylate (ASA). In this article, discussion is made on mechanical properties of PC and modified ASA terpolymer blend.

EXPERIMENTAL

Materials

PC (LV11 NC-010) and an ASA terpolymer (LURAN 778T) were procured from DuPont and BASF, respectively. MA and benzoyl peroxide (BPO) were procured from Loba Chemie, Mumbai, India.

Preparation of grafted ASA

ASA, MA, and benzoyl peroxide were mixed and the resulting mixture then feed into twin screw extruder at a screw speed of 75 rpm and temperature 240°C. The extruded strands were quenched in cold water and palletized. It was reported by some workers that the grafting degree was affected by either reaction time or the loading of MA. At constant loading of MA, the relative grafting was increased with reaction time. At constant reaction time, the

Correspondence to: A. A. Ramteke (amolramteke2004@gmail.com).

relative grafting degree increased with increasing loading of MA.¹² Here an optimum value is taken directly from literature¹³ to study the effect of grafting on the properties of final blend. The details are given in Table I.

The addition of styrene as co-monomer to the melt grafting system of MA could greatly improve the graft degree of MA. It has been shown that the maximum MA graft degree is obtained when the molar ratio of MA to styrene is $\sim 1 : 1$ for the same concentration of MA. Styrene reacts with MA to form SMA copolymer during the melt grafting process and the grafting of SMA leads to improving the graft degree of MA.¹⁶ The purpose of MA grafting on ASA is to introduce reaction sites so that the OH groups on the ends of PC chain might be linked with anhydride group via esterification. This grafting is to be carried out in a twin screw extruder during extrusion called as reactive extrusion.

Determination of degree of grafting of maleic anhydride

The degree of grafting can be determined by back titration procedure. The ungrafted ASA sample (1.0 g) was dissolved in 100 mL acetone, and then 10 mL ethanol solution of NaOH (0.1 mol/L) was added. The mixed solution was refluxed for 30 min under stirring, then back-titrated with HCl (0.1 mol/L) using methyl red as the indicator.¹⁵ The grafted ASA was treated using the same procedure as the ungrafted ASA.

GD was defined as the amount of grafted MA as a percentage of ASA-g-MA and calculated by

$$\text{GD (\%)} = \frac{(V_0 - V_1) \times 10^{-3} \times C \times M}{2W} \times 100$$

where V_0 is the amount of HCl consumed by using pure ASA as reference (mL), V_1 is the amount of HCl consumed by the grafted sample (mL), C is the molar concentration of HCl (mol/L), M is the molecular weight of MA, and W is the weight of sample (g). The degree of grafting obtained was 0.406%. Initially, this MA grafted ASA (ASA-g-MA), ASA and PC in 90/10 composition were melt mixed by varying the weight percent of ASA-g-MA from 1 to 8 wt %. This has done in twin screw extruder from temperature range 180–240°C. The granules were injection molded in dumbbell-shaped samples and mechanical properties were evaluated. The optimum values were obtained at 4 wt % of ASA-g-MA in 10 wt % of ASA (results not shown here). The different blend compositions were made by keeping this ratio constant in each case.

TABLE I
The Different Amount of Material Used for Grafting

ASA in phr	MA in phr	BPO	Styrene
100	3.5	0.1%	2 mL

Blend preparation

After optimization the subsequent blends were also made in twin screw extruder. Blends of PC, ASA, and grafted ASA were prepared by melt mixing the components in a twin screw extruder (Model JSW TEX 30 \acute{a} twin screw, L/D ratio 36 : 1) at 240°C with screw speed of 100 rpm. Before blending, the PC was dried at 100°C for 6 h and ASA is dried at 80°C for 4 h to remove the moisture.

Molding of specimen

Specimens for mechanical property evaluation were made by injection molding of the granules of the blend on L & T Demag screw type machine (Model PFY 40 LNC 4P) at 240–280°C.

Measurements

A Zwick universal tester (Model Z010) was used to measure tensile properties using dumbbell-shaped samples according to the ASTM D638 test procedure. Izod impact strength of the notched specimens was determined on a falling hammer type impact tester (Ceast impactometer) following the ASTM D256 procedure.¹⁷ The storage modulus, loss modulus, and $\tan \delta$ value were measured on DMA tester (Model DMA Q800 V 7.0). Cryogenically fractured surface of the flexural specimens were scanned on Carl Zeiss Smart SEM (Model SMT EVO 50) to examine the dispersion of the modified ASA (MASA) in the PC matrix. The fractured surfaces were coated with silver before scanning.

RESULTS AND DISCUSSION

Tensile strength

Figures 1 and 2 exhibit variations in relative tensile strength σ_b/σ_m (the ratio of tensile strength of PC/MASA blend to that of PC matrix) against dispersed phase volume fraction ϕ_d . The tensile strength of the blends shows marginal decrease on addition of MASA terpolymer. This marginal decrease in tensile strength may be attributed to change in the effective cross-sectional area brought about by the dispersed phase. The stress and strain are highest at the yield point, but due change in cross-sectional area, it leads to neck formation and thereby reduces the tensile strength.¹⁸ At the break, the cross-sectional area further reduced so further lowering of tensile strength

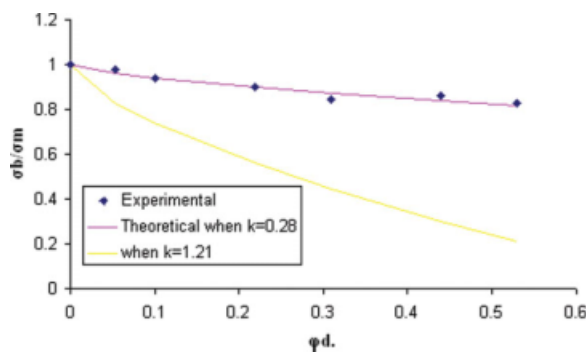


Figure 1 Variation of the relative tensile stress at break σ_b/σ_m of (◆) PC/MASA blends and the Nicolais–Narkis model (—) with $K = 0.28$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

at break than at yield. This indicates that weakening of the matrix polymer structure on account of the decrease in effective matrix cross-sectional area due to the presence of ASA.¹⁹ Similar results were reported in the other elastomer modified blend system.²⁰

Table II exhibits the values of K and α estimated at each volume concentration of the dispersed phase MASA by comparing with tensile strength data with the predictive models, eqs. (1) and (2). Nicolais–Narkis model, eq. (1), shows that the stress concentration parameters were either less than or higher than unity depending on the value of ϕ_d . In Figures 1 and 2, the experimental tensile strength values are compared with the theoretical models eqs. (1) and (2), respectively.

Some theoretical models were used to understand the weakness/discontinuity in the blend structure introduced by the dispersed MASA phase. Similar theories depicted by eqs. (1) and (2) were used in other two phase systems of polymer blends and com-

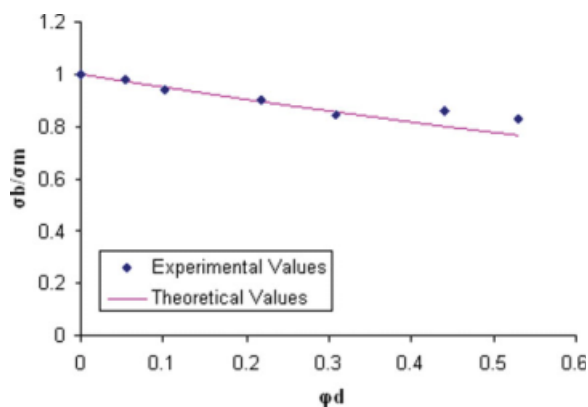


Figure 2 Variation of the relative tensile stress at break σ_b/σ_m of (Δ) PC/MASA blends and the porosity model (---) with $\alpha = 0.50$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Values of Interphase Adhesion Parameter K and Stress Concentration Constant α in PC/MASA Blends

ϕ_d	K	α
0	—	—
0.053	0.42	1.16
0.101	0.29	0.82
0.219	0.27	0.48
0.310	0.34	0.55
0.440	0.24	0.33
0.529	0.29	0.36
Mean value	0.28	0.50

Because of data scatter, average value was estimated excluding some data points, e.g., for both K and α at $\phi_d = 0.053$.

posites too, to analyzed the weakness/discontinuity in the structure.^{18,21} These models assume the blend structure to be no-adhesion type and the tensile property is a function of either the area fraction or the volume fraction of the dispersed phase.^{21,22} Equation (1), that is, a two-third power law model, is the Nicolais–Narkis expression where the area fraction of the discontinuous phase is considered effective. The Nicolais–Narkis model (1) and porosity model (2) were in two phase systems of polymer blends and composites to analyze the structure of blend.

$$\sigma_b/\sigma_m = (1 - K \phi_d^{2/3}) \quad (1)$$

$$\sigma_b/\sigma_m = \exp(-\alpha \phi_d) \quad (2)$$

In eq. (1), the area fraction or the volume fraction of the dispersed phase is assumed to be operative and the interphase interaction parameter K , also known as weightage factor, is a function of the blend structure.^{23,24} The parameter K assumes a value of 1.1 for hexagonal packing of the inclusion in the plane of highest density. For spherical inclusions with poor adhesion $K = 1.21$,^{22,25} whereas $K = 1$ stands for strain consideration. Although $K = 0$ describes the unblended matrix polymer, values of $K < 1.21$ indicates better interphase adhesion; the lesser is the value, the better is the adhesion.²⁶

Equation (2) describes the porosity model, where the nonadhering minor phase is assumed to be in the form of pores/voids in metals, ceramics, or polymer matrices without any contribution to the mechanical properties of the two phase systems.^{27,28} The defects in the structure are reflected in the value of the parameter α , the higher is the value, the higher is the degree of weakness or stress concentration in the structure.²²

In Figures 1 and 2, the values of tensile strength data are compared with the Nicolais–Narkis model, eq. (1), and the porosity model, eq. (2). The data showed good fit with some scattering with the

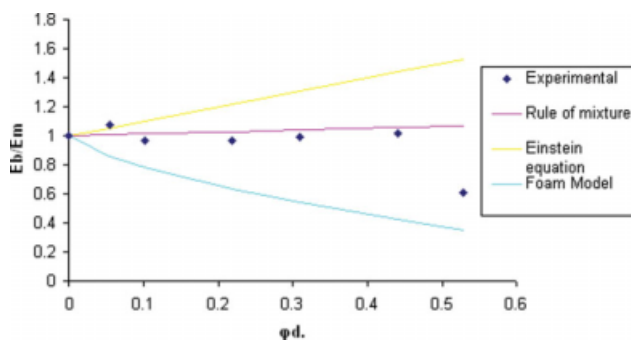


Figure 3 Plot of relative tensile moduli (E_b/E_m) of PC/MASA as a function of volume fraction of disperse phase ϕ_d . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Nicolais–Narkis model, with an average of $K = 0.28$ (Fig. 1). The value of $K = 1.21$ indicates spherical inclusions with poor adhesion and the experimental data points scattered from the curve obtained when $K = 1.21$ (Fig. 1). Nevertheless, the individual data points indicate an extent of good adhesion between the phases. The porosity model, eq. (2), also showed significantly good agreement with the curve for an average of $\alpha = 0.50$, indicating an extent of inter-phase adhesion.

Tensile modulus

The plots of the variation of relative tensile moduli (E_b/E_m) of PC/MASA as a function of volume fraction of disperse phase ϕ_d is shown in Figure 3.

The data were compared with the theoretical values according to the “rule of mixture” as in composites,²⁹ eq. (3), “Einstein equation without adhesion,” eq. (4), and as well as “Foam model,” eq. (5), proposed by Cohen and Ishai.³⁰

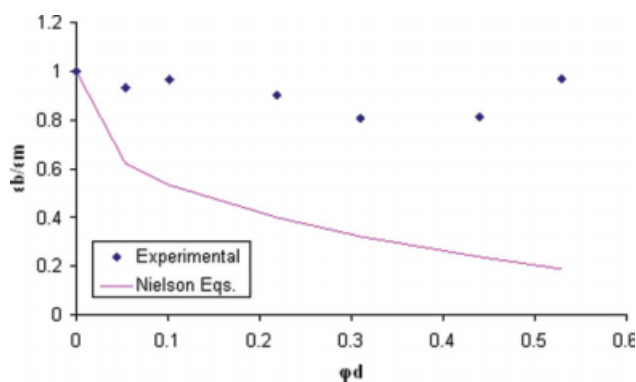


Figure 4 Plot of relative elongation ϵ_b/ϵ_m as function of volume fraction ϕ_d . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

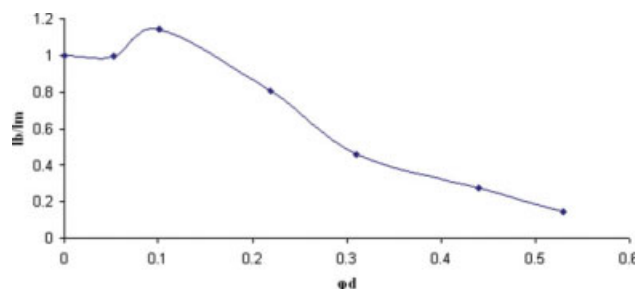


Figure 5 Plot of relative Izod impact strength of PC/MASA versus volume fraction of MASA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

$$(E_b/E_m) = (E_d/E_m - 1) \phi_d + 1 \quad (3)$$

$$(E_b/E_m) = 1 + (\phi_d) \quad (4)$$

$$(E_b/E_m) = 1 - \phi_d^{1/3} \quad (5)$$

In these calculations, the moduli values of the PC (E_m) and the blends (E_b) were estimated from the initial slopes of the stress versus strain curves, whereas the modulus value (E_d) of the MASA was determined at 50% strain. In the foam model, the rubber phase was considered as the noninteracting phase equivalent to a void or pore. The rationale of this is due to the value of the E_d as compared with that of the matrix so that the modular ratio E_d/E_m tends to be negligible, similar to other report.²⁰

The relative modulus data were slightly lower than the “rule of mixture.” This indicate that the tensile modulus deviate negatively from “rule of mixture,” which implies that stiffness of PC decrease with increasing the MASA content.

The value of tensile modulus is highest at $\phi_d = 0.10$, then it continuously decreases with an increase in terpolymer content. The highest value at $\phi_d = 0.10$ may be attributed to lower compatibilization effect. The decreased in tensile modulus may be due to softening of the matrix brought about by the dispersed phase. Here the stiffness of the matrix decreases leading to shear yielding effect as observed in most of the elastomer blend systems.

Breaking elongation

Nielson model for elongation are used for the prediction of results.^{31,32}

$$\epsilon_b/\epsilon_m = 1 - \phi_d^{1/3} \quad (6)$$

The experimental points scattered from the Nielson model, eq. (6), as shown in Figure 4. The elongation of the blend increases in presence of modified ASA terpolymer up to $\phi_d = 0.101$, beyond

TABLE III
Values of T_g of Different Blend Composition Determined from DMA

Composition	ϕ_d	T_g^{PC}	T_g^{BA}	T_g^{ASA}
Polycarbonate	0	154	–	–
PC/MASA5	0.053	156.6	–27	
PC/MASA10	0.101	154.9	–25.8	
PC/MASA25	0.219	153.7	–11.8	123.86
PC/MASA40	0.310	152.2	–31.7	123
PC/MASA70	0.440	151.3	–31.3	123.3
PC/MASA100	0.529	148.6	–32.1	123
ASA terpolymer	1	–	–	118.5
Butyl acrylate	–	–	–37.3	

this point, the decrease was observed. This increase in elongation at $\phi_d = 0.101$ may be attributed to compatibilization effect at this loading where the second phase stretches with the matrix. This implies that PC softened by the MASA facilitating the molecular deformation of the plastics. The modulus data also indicated matrix softening effect by the MASA. Matrix softening also indicates toughening of the PC, which will consume additional energy to break.

Impact strength

Figure 5 shows that the highest impact strength is at $\phi_d = 0.101$. Beyond this point, the impact strength decreases with increasing MASA content. There was 10% increase in impact strength observed. This may be due to modification of interface by the grafting of MA. The MA might be linked with hydroxyl end group, and thus modify the interfacial properties by reducing the tension between PC and ASA. At $\phi_d = 0.101$, the system becomes soften to transfer the stress to the dispersed phase so more energy will be consumed for fracture. Shear yielding may be facilitated at this blend composition.

The variation of impact strength data shows qualitative resemblance with that of the elongation. The increase in impact strength may be attributed to the

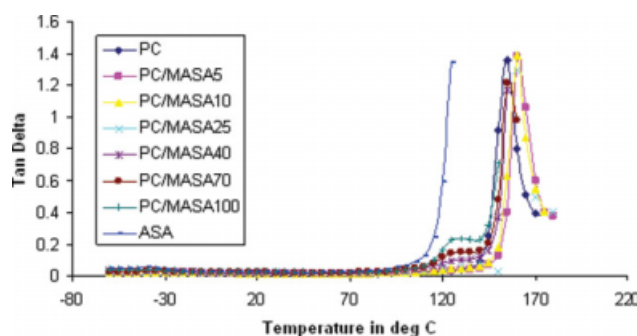


Figure 6 Variation of $\tan \delta$ value with temperature for PC/MASA blend. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

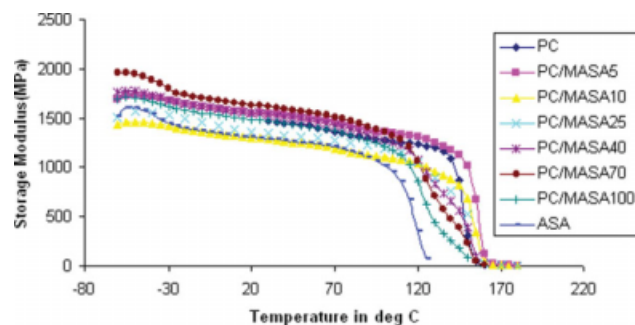


Figure 7 Variation of storage modulus with temperature for PC/MASA blend. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

formation ligament thickness equal to critical thickness T_c in the matrix, which facilitates the shear yielding leading to ductile fracture. The shear yielding may be initiated in the region of high stress concentration, giving rise to local strain in homogeneities.¹⁸ The decrease in impact strength at higher level of rubber may be due to formation of thicker ligament thickness than critical thickness, which caused by coalescence of rubber at higher concentration leading to formation of coarse rubber particle.

Dynamic mechanical properties

DMA measures the stiffness and the mechanical damping or internal friction/thermal dissipation of a dynamically deformed material as a function of temperature. The glass transition temperature of different blend composition is shown in Table III. The loss modulus peak corresponds to the maximum heat dissipation per unit deformation. In addition to T_g , there are other transitions which can be observed using DMA. The lower temperature transitions usually involve motions of side chains and imperfections.³³

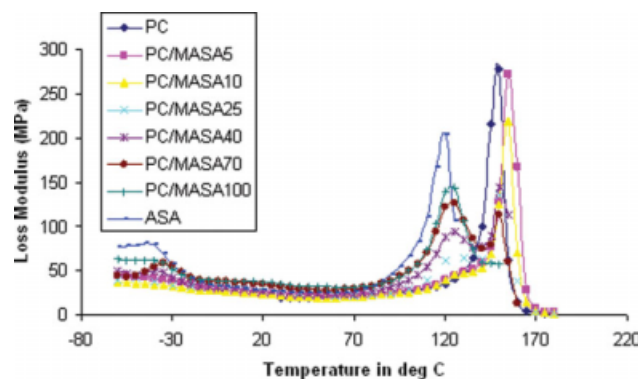


Figure 8 Variation of loss modulus with temperature for PC/MASA blend. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

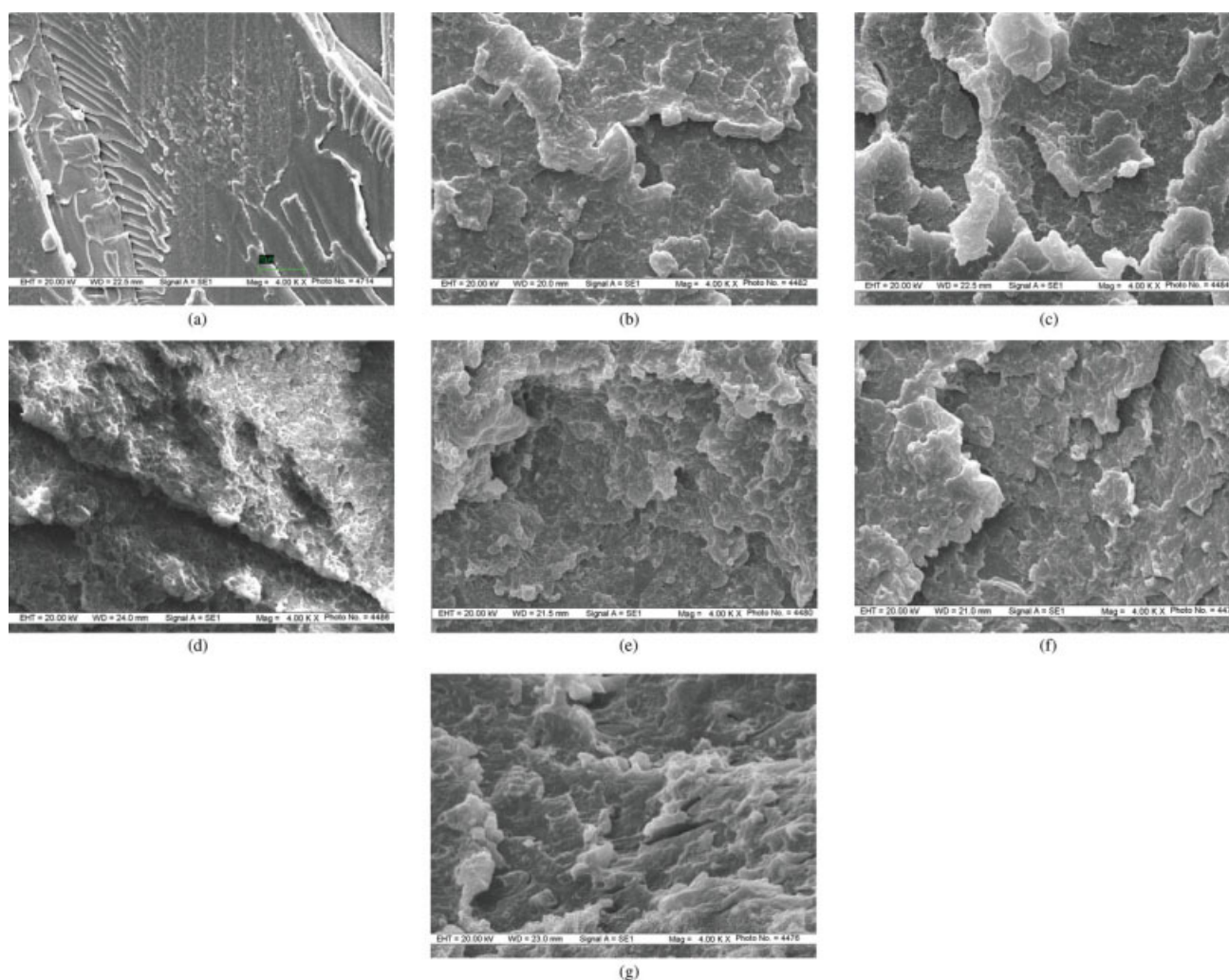


Figure 9 SEM micrographs of notched impact-fractured specimen of: (a) PC, (b) PC/MASA (5 phr), (c) PC/MASA (10 phr), (d) PC/MASA (25 phr), (e) PC/MASA (40 phr), (f) PC/MASA (70 phr), and (g) PC/MASA (100 phr).

The $\tan \delta$ versus temperature plots for modified PC/ASA blends are shown in Figure 6. Characteristic damping peaks are observed for PC and ASA at 158°C and 119°C. These damping peaks are their corresponding glass transition temperature. The primary relaxation of the polymer corresponding to the T_g results from the initiation of the micro-Brownian motion of the amorphous chain. The transition in ASA is due to SAN. As weight percent of MASA increases, the transition peak for PC increases up to $\phi_d = 0.101$ and then decreases continuously. This decrease is consistent with partial miscibility, and may be attributed to reduction in molecular weight of PC during melt grafting by MA. This may also be due to the chemical reaction between MA and hydroxyl end group of PC, which helps to smooth the interface between PC and ASA.

The storage modulus results for modified system are also supportive evidence of partial miscibility.

The storage modulus curve for PC shows single transition, whereas in blends two transitions were observed. The curve at $\phi_d = 0.101$ shows higher reduction in storage modulus than other curves shown in Figure 7. The transitions of butyl acrylate rubber were also observed, it was -37°C for ASA (Table III) and then it decreases continuously with increasing PC content, the decrease was highest at 25 phr indicating that rubber particle becomes stiff at low temperature. This also indicates that low temperature impact in case of 25 phr will be always lower than that of other. The loss modulus versus temperature curves of unmodified and modified blends are also supportive evidence for partial miscibility as shown in Figure 8. The loss modulus is sensitive to many kinds of molecular motions, transitions, relaxation processes, structural heterogeneity, and the morphology of multiphase systems. The peak for blends shows that the

damping characteristic increases with increasing MASA.

Morphology observation

The SEM micrographs for the modified blends show the uniform distribution of MASA in the PC matrix at 25 phr as clearly shown in Figure 9(d). At low concentration of ASA, the stress whitening is observed, it is due to shear yielding. Beyond 10 phr, gross-phase separation is prevalent that may interfere with stress transfer, which hampers impact strength at higher loading. The compatibilized ASA based on MA is very effective in reducing the rubber particle size of dispersed ASA domain. This leads to improvement in tensile ductility and impact strength. But the impact strength decreases on increasing rubber content because the shape of the dispersed phase deformed from spherical to elongated inclusions with significant enhancement in size of the particle. On increasing the MASA, the morphology changes and, at 100 phr, the system shows co-continuous behavior in Figure 9(g).

CONCLUSIONS

Grafting of ASA was carried out by MA to prepare ASA-g-MA, which acts as compatibilizer for PC/ASA system. The optimum value of compatibilizer was found four in 10 parts of ASA as per mechanical evaluation.

The different compositions of compatibilized blends with constant ratio in each case were injection molded and their mechanical, thermal, and visco elastic properties were studied. The tensile strength shows marginal decrease and tensile modulus shows decrease with increase in MASA content. Nicolais–Narkis and porosity models were utilized, which indicates good interface adhesion with minimum value of weightage factor and stress concentration factor. Tensile modulus deviates slightly negatively from rule of mixture indicating reduction in stiffness of PC with increasing rubber content. The elongation at break and impact shows similar trend, both increase up to $\phi_d = 0.101$ and then decrease continuously. The highest value of impact and elongation is observed at $\phi_d = 0.101$. These results were well-supported by visco elastic studies. The $\tan \delta$ peaks and modulus peaks are supportive evidence

of partial miscibility. The SEM micrographs also show uniform distribution of rubber particle due to modification of ASA.

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