Chapter 3

Development of PP/ABS Blends

CONTENTS

The rapid increase in the use of blends has become one of the most prominent areas of the polymer chemistry over the last few decades as described in section one. Blending produces materials with properties superior to those of single polymer. In the present work the blending of PP and ABS has been carried out. Where PP being commodity, semicrystalline thermoplastic offers useful balance of heat and chemical resistance, good mechanical and electrical properties, and processing ease. Whereas ABS is a versatile family of thermoplastics that contains three monomeric constituents: acrylonitrile, butadiene and styrene. Each of these components impart a different set of useful properties to the ABS. Acrylonitrile gives chemical resistance and heat stability, whereas butadiene provides impact resistance and toughness and styrene provides rigidity and processing ease. The resulting PP / ABS blends can have the properties of ABS (toughness and modulus) and PP, which make the blend more cost effective, with good chemical resistivity as well as elongation.

However, PP and ABS are incompatible with each other. The various types of compatibilizers used in the development of PP / ABS blends are discussed earlier and detailed account of PP / ABS blends is given here.

3.1.1 Acrylonitrile- Butadiene- Styrene (ABS)

ABS comprises of acrylonitrile, butadiene and styrene. ABS was developed in past to improve the toughness of styrene – acrylonitrile (SAN) copolymer. It was first introduced in 1946, by Naugatuck chemical company with the trade name Roydlite, A mechanical blend of styrene-acrylonitrile copolymer (SAN) and nitrile rubber (NBR) is known as ABS-type A[1]. There after another type of ABS was introduced in 1950's under the name ABS- type G in the laboratories of Standard oil, B-F Goodrich and U.S. Rubber. This G-type ABS was produced first by emulsion – polymerisation of butadiene of the desired particle size and then it was grafted with styrene and acrylonitrile. These materials showed better performance over type-A material[2 - 4].

More drastic modification of ABS has also been known where replacement of acrylonitrile with methacrylonitrile led to a modified version of ABS known as MABS[5]. Chlorinated polyethylene when added in place of butadiene resulted into acrylonitrile-chlorinated polyethylene - styrene (ACS), whereas replacing PB by EPDM in ABS led to acrylonitrile - ethylene rubber - styrene (AES)[6] .

The wide variety of ABS and ABS based resins available in the market differ in composition, morphology and concentration of individual monomers. The impact property of ABS is strongly affected by the concentration, size and size distribution of rubber particles.

Typical applications of ABS include transport containers, textile spools, parts of office equipment and domestic appliances, housing for television, radio and stereo cases, door and luggage handles, safety helmets, toys and fittings for cars and aircrafts.

3.1.2 Polypropylene (PP)

Polypropylene exists in three forms: amorphous atactic PP (aPP), isotactic PP (iPP) and syndiotactic PP (sPP). Atactic PP is a waxy substance and of little commercial value. The commercial form of PP is 90 – 95 % isotactic. Its production became possible in 1957 after the discovery of Ziegler-Natta catalyst. In 1992 Sumitomo chemical company began small scale production of sPP resin using metallocene induced polymerization of propylene[7]. The advantage of sPP over iPP is that the tensile modulus of sPP is five folds higher than that of iPP[8]. In addition isotactic PP is brittle especially at temperatures below its glass transition temperature ($< 0^0$ C). This brittleness is related to the coarseness of spherulate morphology. The fracture mechanics of the resin shows crazing - cracking mechanism in which the unstable crazing leads to crack propagation in iPP[9, 10]. As a result, in 1954 immediate search for the methods for the improvement of its low temperature impact behaviour was carried out by blending it with PE or elastomers[10].

3.2 Blends of PP

Polypropylene blends constitute the most rapidly growing segments of the plastics industry. Development of PP blends with polyalkenes is the most advance area in blending. The main source of difficulty for blending of PP with other polymers is its immiscibility with other commercial polymers.

The necessary compatibilization leads to the modification of the morphology at micro levels. In many cases, addition of a compatibilizer to PP and engineering resins reduces the crystallinity and on the other hand improves the mechanical properties of the blends. There is increased interest in the development of PP blends with PE, EVAC, PC and other polymers[11 - 13].

3.2.1 Blends of PP / PE

Blends of PP and PE have attracted much attention due to their commercial utility. One of the reasons for adding PE to PP is to improve the low temperature impact behaviour of PP[14-16]. Most of PP/PE blends contain the traditional LLDPE and HDPE. The majority of PP/PE blends are immiscible. The compatibilization of PP/PE blends can be achieved by the addition of compatibilizers such as EPR or EPDM copolymers.

Owing to immiscibility, PP / PE blends show a two-phase structure which results in large strains when stress is applied. However, blending increases the crystallinity, which results in improvement of the mechanical properties[14].

The crystallinity of both polymers changes differently and nonlinearly with composition but highest Young's modulus and tensile strength at break is exhibited at 15 - 20 % incorporation of HDPE[15].

Improved fracture properties of PP/PE blends were reported by Rayner et.al.[16] and Crawford and Dakes[17] when EPR was used as compatibilizer. EPDM and ethylene - butene were also used as compatibilizers for PP/ PE blends, the resulting blends were found to be useful for the making of melt-spun or melt-blown fibres[18, 19].

Kim et.al.[20] have observed high extent of cocrystallization in the whole range of PP and PP-PE random copolymer blends. It was also observed that at more than 2 mol % ethylene content in copolymer, the cocrystallization decreases with increasing ethylene content in blends. Terano et.al.[21] reported increase in tensile elongation, impact strength and crazing resistant and transparency of PP / PP-PE copolymer blends.

3.2.2 Blends of PP/ Polyisobutylene (PiB)

The PiB is miscible with PP. Blends of PP with polyisobutene-1, were reported by Romankevich and Frenkel[22] and Lohse and Wissler[23]. The miscibility was reported to be limited only to amorphous region and lowers down the glass transition temperature of blends. Thus an amorphous polyalkene (PiB or PB) works as plasticizer for PP, which improves the impact strength of PP at low temperature. Blends of PP with polytransoctane (PTO) were reported to show five times higher izod impact strength at - 40 ^{0}C to 23 ^{0}C than PP [24].

3.2.3 Blends of PP / Elastomers

Blends of PP with elastomers constitute a large and commercially important class of resins. Blends of PP with rubbers, thermoplastic alkenic elastomers, chlorinated polyalkenes, styrenic elastomers and, acrylic elastomers which are well known and already commercialised are discussed here.

Blends of PP / Rubber

Elastomeric graft copolymers such as SBR and NBR were found to be valuable for impact modification of PP. The blends with 5 - 20 % of SBR or NBR were reported to show good toughness and better properties for moulding and were relatively free from stress cracking [25, 26].

Blends of PP/ EPR and EPDM

The blends of PP and EPDM are characterised by their high stiffness, high softening temperature, excellent low-temperature modulus and impact strength, dimensional stability, low shrinkage and good mechanical properties in a wide range of temperatures (- 40 to 15 ^{0}C). The first patent application for low temperature impact modification of PP by compounding it with 10 - 60 w % EPR was filed by Schilling from Hercules Powder Company in 1960[27]. There after numerous patents and research papers have been published on PP / EPDM and PP / EPR blends[28-31]. Recently Phan et.al.[30] reported increased interface thickness when polyoxypropylene diamine was added as a compatibilizer in PP / maleated EPDM blends. This was attributed to the imide bond formation at interface, which increases the interface thickness. Cakmak and Cronin[31] and Lin et.al.[32] reported the effect of compositions and processing conditions on the development of PP / EPDM blends. The optical microscopy and X-ray diffraction study of these blends showed increased level of crystallisation.

Blends of PP / Chlorinated Elastomers

In 1990 Ainsworth from Dow Chemical Company patented a blend comprising PP or PE mixed with chlorosulfonated polyethylene. The blends were first partially vulcanised before the addition of inorganic fillers such as MgO, CaO and $CaCO_3$. The resulting systems exhibited good processibility and weld line strength[33].

Blends of PP / Styrenic Elastomers

In early days for effective impact modification the elastomeric graft copolymers, SBR were usually incorporated at about 5 -20 w % into PP blends. Interest in these materials still remains strong. The blends free from brittleness and stress cracking were found suitable for blow moulding of bottles. Blends comprising of 75 - 95 w % PP and 5 – 25 w % uncured elastomers such as PBR and SBR showed high notch impact strength at low temperature[34].

In 1992 Denicolajr and Conboy from Himont Company[35] developed compatibilized PP / SBR blends containing 10 - 90 w % of PP and 2 - 40 w % of either SBR, SBS or an acrylic elastomer and PP grafted with styrene and or acrylonitrile or methacrylate. These compounds were found useful as stand-alone (without fillers) structural materials. Tsuchida et. al.[36] have reported blends of PP and hydrogenated SBR, which exhibited 220 kg / cm^2 tensile strength and 900 % elongation at yield and improved flexibility.

Blends of PP / acrylic Elastomers

Blends of PP with acrylic copolymers, having good strength and heat resistance were claimed in 1987 by Saltman from Dupont de Nemours Company[37]. These blends were prepared by reactive processing of 35.7 w % of PP, an ionomer (ethylene - butylacrylate - acrylic acid Zn salt) and EBA – GMA copolymer.

3.2.4 Blends of PP / EVAc

In 1960 Monsanto Company developed the first blend of PP and ethylene vinyl acetate (EVAc) to improve dyeability, flexibility and toughness of PP[38]. The blends comprising 10 - 90 w % of PP, 5 - 60 w % of EVAc and 5 - 50 w % of PEO were reported by Sanchez et. al.[39]. The blends were reported to have good mechanical properties and reduced O_2 permeability suitable for food packaging. In another contemporary patent from McGill University, extrusion of PP with ethylene - vinylalcohol and maleated propylene (PP-MA) sheets was reported to result in the blends with reduced permeability for gases or liquids which was reported by Kamal et.al.[40] in their studies.

In 1991 Koyama et.al. from Tonen corporation have derived a monodispersed compatibilizer from living polypropylene or ethylene - propylene random copolymer and acrylic derivatives, which was further blended with PP and PVAc[41].

3.2.5 Blends of PP / PVC

The first PP / PVC blend was reported in 1961 by Rosenfelder and Rosen from Dublon Company[42] in which PP was blended with 5 - 50 w % of PVC. In 1963, high impact strength PVC useful for pipe or electrical insulation was obtained by blending PVC with 5 w % of PP and 5 w % of MMA butadiene - styrene copolymer[43]. Compatibilized PP / PVC blends with 1 - 40 w % of PP developed in 1982 were reported to have good mouldability and high HDT[44].

3.2.6 Blends of PP / PA

Polyolefin / polyamide blends are of three types

(i) blends with smaller percentage of polyolefins which can improve the impact strength of PA.

(ii) blends with 2 : 3 to 3 : 2 ratio of polyolefins to polyamide which reduce water absorption of PA and improve impact strength.

(iii) blends with smaller percentage of PA which show higher rigidity.

In Dainippon's patent polyamides were toughened by the addition of PP or maleated PP which was reported by Taguchi and Mori[45].

Alloys of PA with PP reduce water migration and increase notch impact strength. Reactive compatibilization of 70 w % of PP with 30 w % of PA-6 in the presence of maleic anhydride grafted on either EPR or SEBS elastomers was reported by Utracki and Sammut[46]. Rosch and Mulhaupt[47], Xie et.al.[48] have reported PP and Ny-6 blends compatibilised through PP-g-GMA. The blends were reported to exhibit microphase separated structure and the interphase was reported to be a graft copolymer resulted from the reaction of oxirane ring of GMA and -NH_2 group of Ny-6. Sathe et.al.[49] reported the blends of PP/ Ny-6, which were compatibilized through maleated PP and PP-g-butylacrylate. The blends upto 30 w % of Ny-6 were reported to exhibite better impact strength, flexural modulus and tensile properties. Tornell[50] reported compatibilisation of PP / Ny-6 blends on the use of maleated SEBS. They have reported thickness of interphase layer to be 15 nm and good mechanical properties of the blends.

3.2.7 Blends of PP / Polystyrene (PS) and styrenic copolymer

Blends of PP / PS

In the year 1971 Ogawa et.al.[51] from Sumitomo Chemical Company developed blends of PP with 3 - 30 w % of PS. The blends useful for soda-straw tubes exhibited pearly lustre. In a patent by Morrow et.al.[52] from Rutgers state University in 1990 in which uncompatibilized polyalkene / styrene blends derived from recycled HDPE and or PP with PS were reported to show good mechanical properties. The improved properties were attributed to the presence of cocontinuous morphology and rheological properties. Radonjic et.al.[53] reported compatibilization of PP / PS blends upon the use of poly(styrene - butadiene - styrene) block copolymer. SEM studies of these blends showed the reduction in the size of dispersed phase PS on the addition of block copolymer. It was observed that incorporation of SBS decreases the tensile strength and the young's modulus but elongation at yield and notched impact strength increases. Matos et.al[54]. reported blends of PP / PS which were compatibilized with styrene - ethylene - propylene block copolymer. The interface of the blend was reported to increase with the addition of such interfacial agent.

Anionically synthesised SBS block copolymers as a compatibilizer could bring compatibilization in the blends of PP and PS. The blends were reported to show improved impact strength and tensile strength[55]. Improvement in impact strength from 3.2 to 10.9 kg cm/cm was reported on compatibilization. Xu and Lin[56] reported compatibilization of PP/ PS blends by PP-PS block copolymer. The blends were reported to exhibit smaller size of dispersed particles and improved mechanical properties

Blends of PP / SBS / HIPS

Compatibilised blends of PP and HIPS have been developed by Castelein[57]. Addition of 17.5 w % of SBS block copolymer improved the impact strength of PP / HIPS blends upto 12.5 kg cm / cm.

Blends of PP / SAN

Ilenda et. al.[58] have reported the use of 15 w % of PP-g-(MMA-EA) as a compatibiliser in PP / SAN blends, which exhibited 0.37 MPa tensile strength. Higher concentration of compatibilizer was reported not to lead to further improvement in mechanical properties.

Blends of PP / SEBS

Anionically synthesised di or tri block SEBS was reported to be compatible with PP. The blends were reported to show increased resistance to crazing and also increased impact strength. The impact strength was reported to increase upto 29 kg-cm/ cm for 45 / 55, SEBS / PP blends[59].

3.2.8 Blends of PP / Polyester

Ilenda et.al.[60] reported compatibilization of PP and PET blends using PP-g-(MMA-EA) compatibilizer. This is attributed to the partial miscibility between acrylate groups of graft copolymer and PET. Compatibilization of 70 / 30, PP/ PET blends on the addition of 15 w % of compatibilizer increased tensile strength from 0.23 MPa to 0.27 MPa.

Xanthos et.al.[61] have reported that the physical properties of PP / PET blends improve on the addition of PP-g-acrylic acid. The PP-g-acrylic acid acts as reactive compatibilizer for PP / PET blends. The increase in compatibility was attributed to the decrease in the particle size of dispersed phase, which resulted into improved mechanical properties. Tensile strength of 65 / 35, PP / PET blend was reported to increase from 34.4 to 39.9 MPa on the addition of PP-g-acrylic acid. Ballauri et.al.[62] reported compatibilization of recycled PET/PP blends using functionalised SEBS-g-maleic anhydride. The blends were reported to show improvement in tensile strength and thermomechanical resistance.

Blends of PP / PBT were first reported in 1974 by Seydl and Strickle from BASF[63], which contained 10 - 30 w % of PP. The blends exhibited good mouldability and high electrical tracking resistance.The blends of PP / PBT generally show good processibility, toughness, rigidity, strength and dimensional stability.

3.2.9 Blends of PP / Liquid Crystal Polymers

Owing to the cost, PP blends only with relatively small amount of LCP have been developed. Usually these are non-compatibilized but aimed for the improvement of either processibility or rigidity of blends. It has been claimed that addition of LCP to a variety of thermoplastic resins such as PP, PPS, PC, PEST, PPE reduces the melt viscosity and facilitates extrusion and injection moulding of LCPs[64, 65]. The contribution of LCP depends on the blend's morphology of unoriented spherical suspension of LCP in PP. The reinforcing effect depends very much on the orientation of the LCP crystals in PP during the formation stages. For this reason, mostly uniaxially oriented films, fibres and mouldings have been prepared from these blends[66, 67]. Scaffaro et.al.[68] reported blends of PP / LCP using PP-g-oxazoline as a compatibilizer. The blends exhibited good tensile strength, young's modulus and elongation.

3.2.10 Blends of PP/ PC

Addition of polycarbonate to PP leads to enhancement in the crystallinity of PP and a small increase in the crystallisation temperature. Blends of PP and PC are still in an early stage of development. Ilenda et.al.[69] have demonstrated the formation of compatibilized blends of PP and PC using PP-g-MMA - EA as the compatibilizer. The compatibilization was attributed to the possible miscibility between PMMA and PC phases. Addition of 15 w % of compatibilizer to the 70 / 30 PP / PC composition increased the tensile strength of blends from 0.233 to 0.308 MPa.

Overall the various types of PP based blends have been reported to show improvement in impact strength, tensile strength, and modulus properties. The use of compatibilizer has been reported to show better miscibility of phases and mechanical properties.

3.3 Blends of ABS

Various commercial polymers such as PVC, PC, Polyester and PA have been used for blending with ABS to improve processibility, flame resistance and good weatherability of ABS.

3.3.1 Blends of ABS / PVC

Blends of ABS and PVC have great commercial importance. Good properties of these systems originate from the miscibility between PVC and SAN part of ABS containing at least 20 w % of acrylonitrile. The blends also show the most interesting complementarily properties of two principal polymeric ingredients. In spite of the limited miscibility, for the control of morphology use of acrylic compatibilizers is desirable. The blends offer excellent processibility, high impact strength, UV stability, flame resistance and weatherability.

In 1959 Grabowski and Irvin from Borg-warner Corporation reported blends of ABS and PVC with high tensile strength, hardness and impact strength[70].

Kumabe et.al.[71] have developed PVC / ABS blends with 5 - 30 w % of MABS. The blends were reported to have good transparency and impact strength. Blends of 20 - 80 w % of PVC and polybutadiene grafted with styrene, methylmethacrylate and maleic anhydride were reported by Dufour[72] and Meredith and Ferguson[73] and showed good flame retardance, HDT and impact strength. Dufour[72] has developed ABS / PVC blends by using methyl methacrylate - styrene - acrylonitrile grafted polybutadiene or maleated styrene - methyl methacrylate - butadiene copolymer as compatibilizers. Takagi et.al.[74] have reported ABS / PVC blends with a graft copolymer containing 50 - 85 w % of polybutadiene and methacrylate, styrene and divinyl benzene copolymer. The mouldable alloys were reported to show high impact and good transparency. Hong. et. al.[75] reported ABS / PVC alloys compatibilized with polyethylene rubber and nitrile rubber. These compatibilizers increased the toughness of the blend from 8 kg-cm / cm to 14-18 kg-cm / cm.

3.3.2 Blends of ABS / PC

Bisphenol-A derived polycarbonate (PC) was invented in 1958 and ABS was invented in 1946, whereas the first easily mouldable ABS / PC blend was developed in the 1960's[76]. Grabowski et. al.[77] from Borg-Warner Company blended PC with 10-70 w % of ABS and a butadiene-g-acrylate elastomer in a Banbury mixer at 210^0 C. In 1980's several patents described three - component ABS / PC / PEST alloys of great commercial interest. Bier and Indner[78], Neuray et.al.[79] and Serini et.al.[80] have reported these type blends.

Giles and Scasserath[81] reported blends with 60 w % of ABS, 30 w % of PC and 10 w % of PMMA having excellent weatherability and impact strength. In 1992 Rawlings and Vilasagar from General Electric Company[82] patented a low-gloss mouldable blend of ABS and PC.

ABS / PC blends are amorphous and show good dimensional accuracy, low distortion and shrinkage, low moisture absorption, high softening point, stiffness and hardness comparable to that of PC. However, owing to the PC content, the blends have limited resistance to hydrolysis. Presence of ABS imparts opacity to the blends.

When ABS / PC blends were prepared in the presence of potassium titanate, the materials showed improvement in thermal properties[83]. ABS / PC blends of various compositions were analysed by DMA, IR spectroscopy and were reported to show partial phase separation and miscibility[84]. When PC was compatibilized with maleated modified ABS, improvement in morphology and mechanical properties was observed by Balakrishnan and Neelkantha[85].

3.3.3 Blends of ABS / PA

Blends of ABS and PA are divided in three categories

(i) Blends with smaller amount of ABS for the toughening of PA without compatibilizer.

(ii) Blends with equal amount of ABS and PA for good mechanical properties without use of compatibilizer.

(iii) Blends containing large amount of PA, with compatibilizer.

The main uses of ABS / PA blends are in automotive, chemicals, electricals, electronics, consumer and sport industries, lawn and garden equipments[86].

The first blend of ABS with PA was reported by Grabowski[87] in which 10 - 60 w % of ABS was blended with PA-6. These blends showed good tensile strength, elongation, hardness and stability during moulding. In 1987 one of the most successful PA / ABS blend was introduced by Monsanto Company under the trade name Friutm –1000[88]. In the patent by Fox et.al. from General Electric Company[89] in 1984, blends of amorphous copolyamide(s) and ABS in the ratio 1 : 9 to 9 : 1 were reported to show improvement in impact properties over those of PA. Commercial grades of ABS with high rubber content were modified by reactive extrusion with either maleic anhydride or fumaric acid and then melt blended with PA-6. The blends were reported to exhibit morphology with PA as matrix and ABS forming fine dispersion[90]. The composition was reported to improve the izod impact strength significantly. ABS / PA blends developed by Kudva et. al.[91] which were compatibilized using various acid functionalised styrene – acrylonitrile and acrylate copolymers. The compatibilized blends were reported to show good ductility even at low temperature. Majumdar et.al.[92] also reported ABS / Ny-6 blends using various compatibilizers.

3.3.4 Blends of ABS / PEST

The thermoplastic polyesters (PEST) are dominated by two resins, polyethylene terphthalate (PET), and polybutyleneterphthalate (PBT). Blends of ABS and PEST are also immiscible and require compatibilization. In these blends compatibilizer plays the additional role of an impact modifier. The morphology of the blends depends on the ingredient concentration, their rheological properties as well as the compounding and processing conditions. In most of the cases PEST forms the matrix in which ABS and impact modifier are dispersed[11].

The ABS / PEST alloys show excellent mouldability, low post moulding shrinkage and wrapage, stress-crack resistance, high gloss, high temperature stiffness, toughness and mechanical strength. Their applications include electronics, automotive and electrical industry, as well as business and household equipment manufacturing.

The blends of ABS with PET were reported by Sauers and Barth[93] from Union Carbide Company in 1968 where PET was blended with rubber - modified polyacrylates or methacrylates to improve its notch impact and embrittlement resistance. In 1977 Gergen and Davison[94] from Shell Oil Company reported hydrogenated styrene - butadiene - styrene tri-block copolymer (SEBS) as a compatibilizer for PBT / ABS blends. In 1987 Orikasa and Sukazume[95] from Nippon Petrochemicals described blends of PBT with ABS modified with incorporation of maleic anhydride or glycidylmethacrylate. The alloys showed good heat and notch impact resistant properties. In 1989, Sumitomo Naugutuck Company[96] reported blends containing 10 -90 w % of PPE, 8 - 88 w % of ABS and 1 - 30 w % of an ABS-type graft copolymer having vinyl groups at chain end which are responsible for good processibility and show improved impact resistance.

3.4 Work done on PP/ABS blends

PP - ABS blends were reported by Markin and William[97] in 1980. They studied the blend compatibility through melt viscosity measurements. They have reported not much improvement in mechanical properties due to immiscibility of PP and ABS. In 1990 Gupta et.al.[98] reported maximum melt viscosity at 10 w % of ABS in PP / ABS and PP/ ABS / PE blends. Not much improvement in tensile and impact properties was reported. Later in the year 1993 Frounchi and Paul[99] reported SEBS as a compatibilizer for PP/ABS blends, but no drastic improvement in mechanical performance was observed in this study also.

Several patents[100-110] are also available for PP / ABS blends. In 1982 TDK Electronics Co.[100] announced the blends of PP / ABS using ethylene-vinylacetate as a compatibilizer. The blend with 72:28 PP/ABS ratio was reported to show 22 kg cm / cm impact strength and 380 kg / cm^2 tensile strength. Later on Yazaki et.al[101] reported PP / ABS blends using ethylene -propylene block copolymer as a compatibilizer. The blends were useful for refrigerator panels and automobile bumpers. Go et.al.[102] reported PP / ABS blends with good moulding, heat resistance and impact strength, when maleated PP was used as compatibilizer. Ezaki and Aibe[103] reported compatibilization of PP / ABS blends using maleic anhydride modified PP and AN - HPMA - St copolymer as third component, The blends showed 7.3 kg-cm/cm impact strength. Aibe[104] reported PP / ABS blends with excellent impact resistance when maleated PP was used as compatibilizer and AN – diethyl amino ethylmethacrylate - St as a cocompatibilizer. The blends were reported to have 12.4 kg cm / cm impact strength. Another PP / ABS blend was reported by Yamamoto and Aibe[105], where ethylene - propylene block copolymer was used as a compatibilizer. The blends were reported to have 15 kg-cm / cm of impact strength. In 1995 Kawai[106] from Hitachi Chemical Company patented blends of PP/ABS and maleated PP as compatibilizer, which exhibited tensile modulus of 970 MPa and good impact and solvent resistance.

Present Work

We have undertaken the compatibilization of PP/ABS blends using PP-g-acrylic acid, which can also work like anhydride functionalized PP (PP-g-MAH) and can show a compatibility with ABS.

The other compatibilizer we choose is PP-g-2-HEMA in which acrylates are miscible with ABS, which is discussed later.

Third compatibilizer we choose to compatibilize PP / ABS blends was PP-g-St-AN, in which the one of the segment of graft copolymer St-AN itself is one of the major part of the second blend component ABS. Which can act better compatibilizer.

3.5 Experimental

Materials

The **isotactic polypropylene (iPP)** of M0030 Koyelene grade with density 0.93 g/cm^3 and melt flow index 10 g / 10 min was supplied by Indian Petrochemicals Corporation Ltd., Vadodara, India. Before blending PP was dried in hot air oven at 70^0 C for 12 hrs.

Acrylonitrile - Butadiene - Styrene (ABS) of 100N grade with 1.05 g / cm^3 density and melt flow index 10 g / 10 min was supplied by Bayer-ABS India Ltd. Vadodara, India, and was dried in hot air oven at 70^0 C for 12 hrs.

Compatibilizers **PP-g-acrylic acid**, **PP-g-2-HEMA** and **PP-g-St-AN** were also dried in hot air oven before extrusion.

Blend Preparation

Polypropylene, compatibilizers and ABS were dried in hot air oven at 70^0 C for 24 hrs prior to extrusion. The blends were prepared by melt extrusion technique using Brabender single screw extruder with L/D ratio 20. All the blends were prepared by two step mixing technique. In first step polypropylene and compatibilizer (1:1 w ratio) were premixed in the extruder keeping the temperature of 4 zones at 190 -200 - 210 - 220^0 C and screw speed at 50 rpm. In the second step the resultant mixture was palletised and calculated amount was mixed with ABS and PP in the extruder with screw speed 50 rpm and keeping the zone temperatures at

200 -220 - 230 - 225^0 C for PP rich compositions and 220 - 230 - 250 - 240^0 C for ABS rich compositions. Various blend compositions prepared are given in **Table-3.1.** The extrudates were cut into pallets. The blend pallets were injection moulded using ARBURG *allrounder* 220 - 90 -350 injection moulding machine to obtain the test specimens for the measurements of mechanical properties. The test specimens were prepared as per the ASTM standards.

TABLE 3.1 Composition of PP / ABS Blends

No.	PP/AB/ Compatibilizer	No.	PP/ABS/ Compatibilizer	No.	PP/ABS/ Compatibilizer	No.	PP/ABS/ Compatibilizer
1	100 /0/0	9	90/10/2.5	15	90/10/5	21	90/10/7.5
2	90/10/0	10	85/15/2.5	16	85/15/5	22	85/15/7.5
3	85/15/0	11	75/25/2.5	17	75/25/5	23	75/25/7.5
4	75/25/0	12	25/75/2.5	18	25/75/5	24	25/75/7.5
5	25/75/0	13	15/85/2.5	19	15/85/5	25	15/85/7.5
6	15/85/0	14	10/90/2.5	20	10/90/5	26	10/90/7.5
7	10/90/0						
8	100/0/0						

Compatibilizers: PP-g-2-HEMA; PP-g-acrylic acid and PP-g-St-AN

3.6 Characterisation

Morphology

The morphology of room temperature fractured surfaces etched either with methyl ethyl ketone (MEK) for ABS extraction or hot xylene for PP extraction was examined using scanning electron microscope (SEM) (Leica Cambridge, UK Stereoscan) at 10 kV. The samples were gold coated (50 μm thick) using automatic sputter coater (Polaron equipment Ltd., USA) to avoid surface charging.

Mechanical Properties

Tensile Properties

Tensile properties of the dumbbell shape test specimens having the dimensions of the narrow portion 60 x 12.70 x 3.2 mm were measured according to ASTM D 368 procedure. At least 5-6 specimens were tested for each sample. The specimens which do not break between pre-determined gauge marks or that break at some obvious fortuitous flow were discarded. All the testing was carried out at 50 mm / min cross head speed. Stress-Strain curve, young's modulus, elongation at yield and break, tensile strength at yield and break were obtained from the Instron tester attached to computer.

Izod Impact Strength

The test samples with the dimensions 64.0 x 12.8 x 3.2 mm and 0.25 mm notch radius were used for the izod impact strength measurements. The measurements were carried out according to ASTM D 256 method and at least 5 to 6 individual test specimens of each sample were tested to obtain the average impact strength.

Flexural Strength

Flexural measurement was carried out according to the method described in ASTM D 790. A three point loading system with a central loading on a singly supported beam was used for the measurements. The dimension of test sample was 64.0 x 12.8 x 3.2 mm. During testing the rate of the crosshead motion was kept at 2.8 mm / min. At least 5 - 6 individual determinations of flexural strength values were made on each sample.

3.7 Results and Discussion

Immiscibility between polymer components is responsible for the poor morphology and mechanical performance, which are the major hurdles for the development of high performance blends. Therefore, improvement in the compatibility of immiscible pairs is a major challenge to the technology to obtain blends with desirable properties[10-13].

As discussed earlier various methods such as the introduction of strong specific interactions such as hydrogen bonding, ion dipole interaction, ion-ion interaction, intermolecular repulsive interaction have been used for better compatibilization of polymer blends. The formation of interpenetrating network and cross linking and the addition of block or graft copolymers in blends is similar to the emulsification of oil in water using surface active agents[13-15].

3.7.1 Compatibilization of PP / ABS blends using PP-g-acrylic acid

Blends of PP/ABS are totally immiscible, and need compatibilization to bring miscibility. In this study various PP based graft copolymers such as **PP-g-acrylic acid**[111], **PP-g-2-HEMA** and **PP-g-St-AN** have been used as compatibilizers. The compatibilization effect was measured through the study of mechanical properties particularly impact strength and morphology.

Grafting of acrylic acid on PP through solution polymerization was resulted into 7.2 % of grafting which was determined by a method described by Pedram et.al.[113]. This PP-g-acrylic acid was further used for the compatibilization of PP/ ABS blends. The different compositions of blends prepared for study are given in **Table-3.1**. The blends were further characterised for their morphology and mechanical properties.

Morphology

As expected blends without compatibilizer exhibited coarse and heterogeneous dispersions of the phases as seen in SE micrographs of PP/ABS blends before the extraction of ABS dispersed phase (**Fig. 3.1.a**). Polypropylene rich binary blends exhibited coarsely dispersed ABS particles in PP matrix. Finer and homogeneous dispersion of ABS particles in blends was observed when Pp-g-acrylic acid was added to the blend (**Figure 3.1.b**). More or less cocontinuous two phase structure was

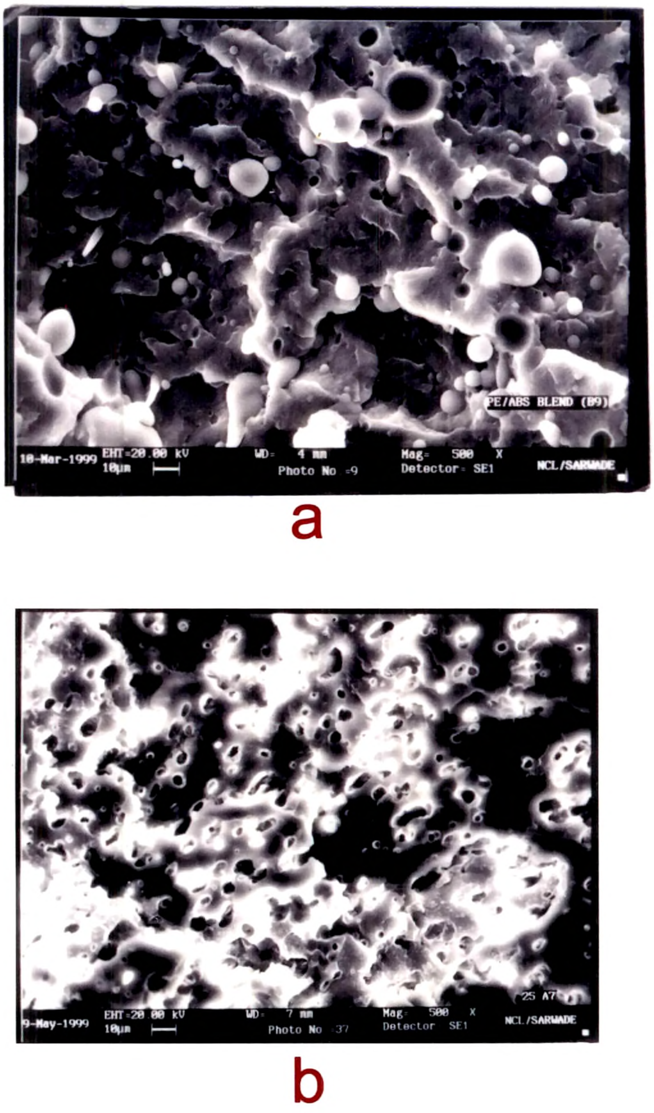


Fig. 3.1 SE micrographs of impact fractured surfaces of PP / ABS blends

a: 90 / 10 , PP / ABS binary blends

b: 90 / 10 / 2.5 , PP / ABS / 2.5 % PP-g-acrylic acid

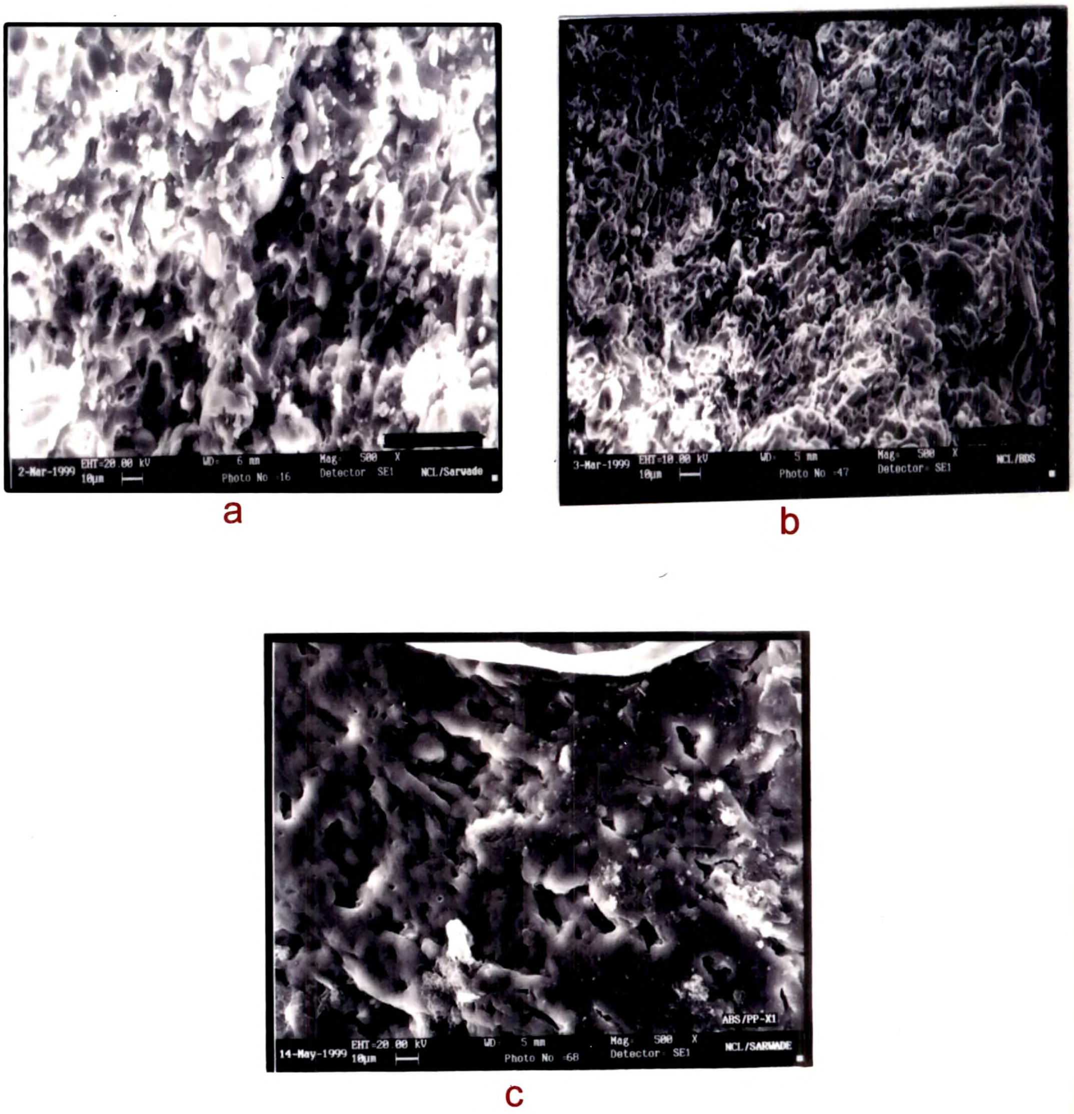
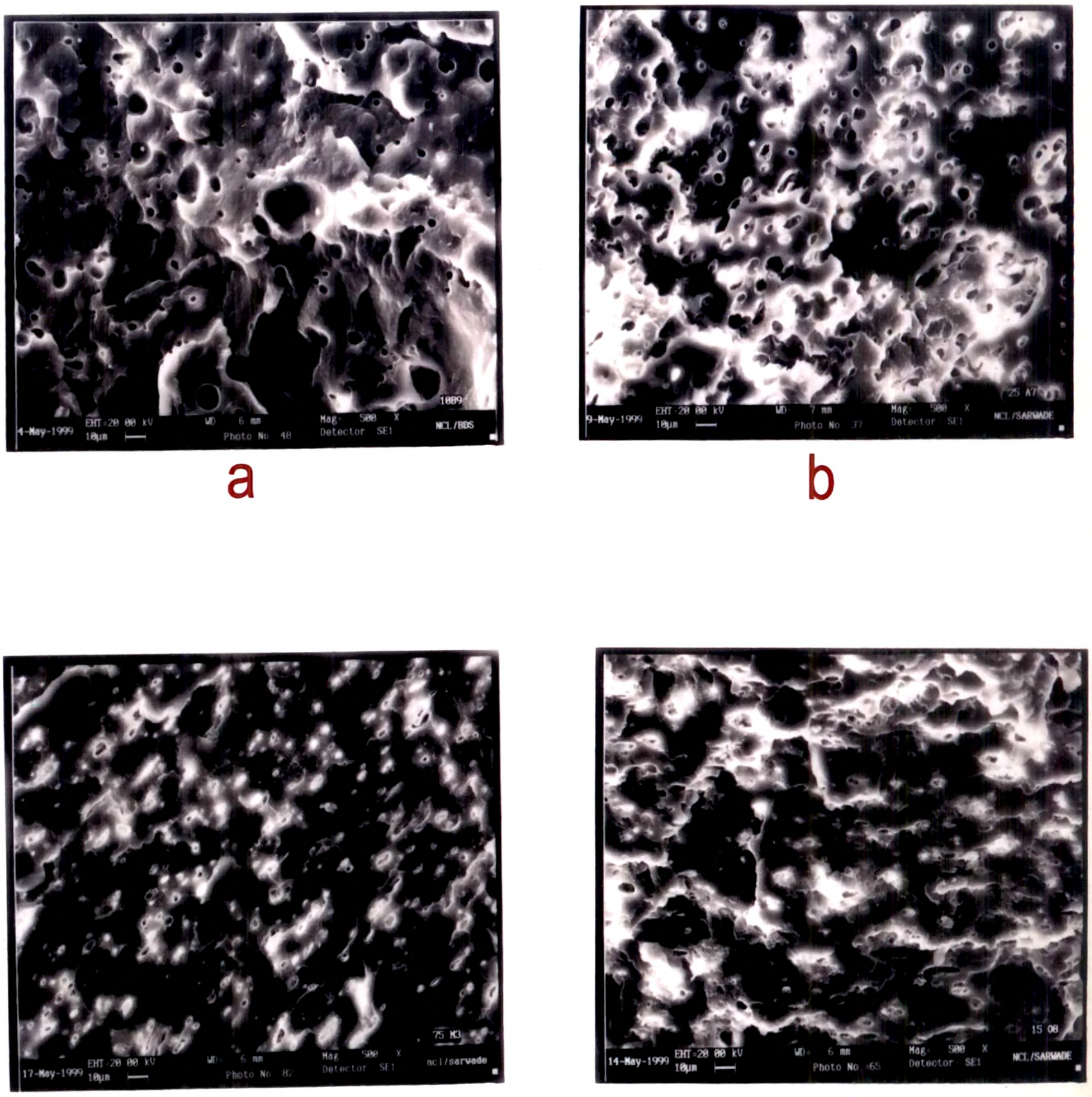


Fig. 3.2 SE micrographs of impact fractured surfaces of ABS rich blends

a: 15 / 85 , PP / ABS binary blends without extraction

b: 15 / 85 , PP / ABS binary blends after extraction of PP in hot

c: 15 / 85 / 2.5 ,PP/ ABS / 2.5 % PP-g-acrylic acid ,after extraction of PP in hot xylene



a

b

c

d

Fig. 3.3 SE micrographs of impact fractured surfaces of PP/ ABS / PP-g-acrylic acid blends after extraction of ABS in MEK

a: 75/ 25 / 0 ; **b**: 75/ 25 / 2.5 ; **c**: 75/ 25 / 5 ; **d**: 75/ 25 / 7.5

observed in the micrographs before (**Fig3.2a**) and after (**Fig. 3.2 b**) extraction of PP by hot xylene from ABS rich blends. Cocontinuous structure was also observed even after compatibilization (**Fig. 3.2 c**).

The compatibilization effect of PP-g-acrylic acid is illustrated in **Figures 3.3.a-d.** The marginal decrease in particle size and increase in particle homogeneity was observed upon addition of 2.5 to 5 w % compatibilizer to PP/ABS blends. **Figure 3.3.a** shows the larger and coarsely dispersed cavities developed due to the extraction of ABS from 75/25, PP/ABS uncompatibilized blends. Whereas the micrographs for the blends with the same composition along with 2.5 and 5 w % PP-g-acrylic acid show smaller and well dispersed and more uniform cavities created after the extraction of ABS in MEK. This indicates that PP-g-acrylic acid reduces the interfacial tension between PP and ABS phases and decreases the size of dispersed particles. Increased compatibilizer concentration at interface helps in effective stress transfer between the dispersed phase and continuous phase. Increase in the compatibilizer concentration from 2.5 to 5.0 w % showed marginal changes in the morphology. Further increase in the concentration of compatibilizer (7.5 w %) did not show any effect on the particle size indicating that 5 w % of PP-g-acrylic acid is sufficient to decrease the interfacial tension between the two phases. Further addition does not contribute to the interfacial properties due to the presence of excess of compatibilizer in the bulk in the form of aggregates and not at the interface. However, unusual increase in the size of dispersed particles was observed in these blend compositions. The size of the ABS domains measured from the SE micrographs is expressed in different ways, such as

$$\overline{D_n} = \frac{\Sigma N_i D_i}{\Sigma N_i} \qquad (1)$$

$$\overline{D_w} = \frac{\Sigma N_i D_i^2}{\Sigma N_i D_i} \qquad (2)$$

and

$$\overline{Dvs} = \frac{\Sigma D_i^3}{\Sigma D_i^2} \qquad (3)$$

where, N_i is the number of domains, D_n is the number - average diameter and D_{vs} the surface -area-average diameter. The polydispersity index, which is a measure of domains size distribution, is calculated from the following equation

$$PDI = \overline{D_w} \,/\, \overline{D_n} \qquad (4)$$

The number average diameter $\overline{Dn}$, weight average diameter $\overline{Dw}$ and surface area average diameter $\overline{Dvs}$ were calculated and were used for the determination of polydispersity index PDI. The results are given in **Table-3.2.** The polydispersity plots for the blends containing 85 and 75 w % PP and different concentrations of compatibilizer are given in **Figure 3.4.** The uncompatibilized binary blends show the broader particle size distribution of ABS domains into PP. With incorporation of compatibilizer, the distribution of particle size becomes narrow and the size of the dispersed ABS particles also decreases. Further increase in compatibilizer concentration may not efficiently contribute to the interface phenomenon as the critical concentration of it occupies the interface and excess concentration may form micellar aggregates in the bulk. Similar observation was reported by Asaletha et. al.[113] and Thomas and Prud'Homme[114] for PP / NR blends.

TABLE 3.2 Particle size and polydispersity index in PP/ABS blends

PP / ABS / PP-g-acrylic acid	$\overline{Dn}$ (μm)	$\overline{Dw}$ (μm)	$\overline{Dvs}$ (μm)	PDI
90/10/0	7.50	8.33	11.0	1.24
90/10/2.5	5.62	7.07	10.05	1.13
90/10/5	5.43	6.74	9.69	1.11
90/10/7.5	6.15	7.96	10.15	1.14
75/25/0	6.9	8.12	10.12	1.31
75/25/2.5	6.44	7.23	10.3	1.14
75/25/5	6.30	7.46	10.3	1.15
75/25/7.5	6.80	8.67	10.3	1.27

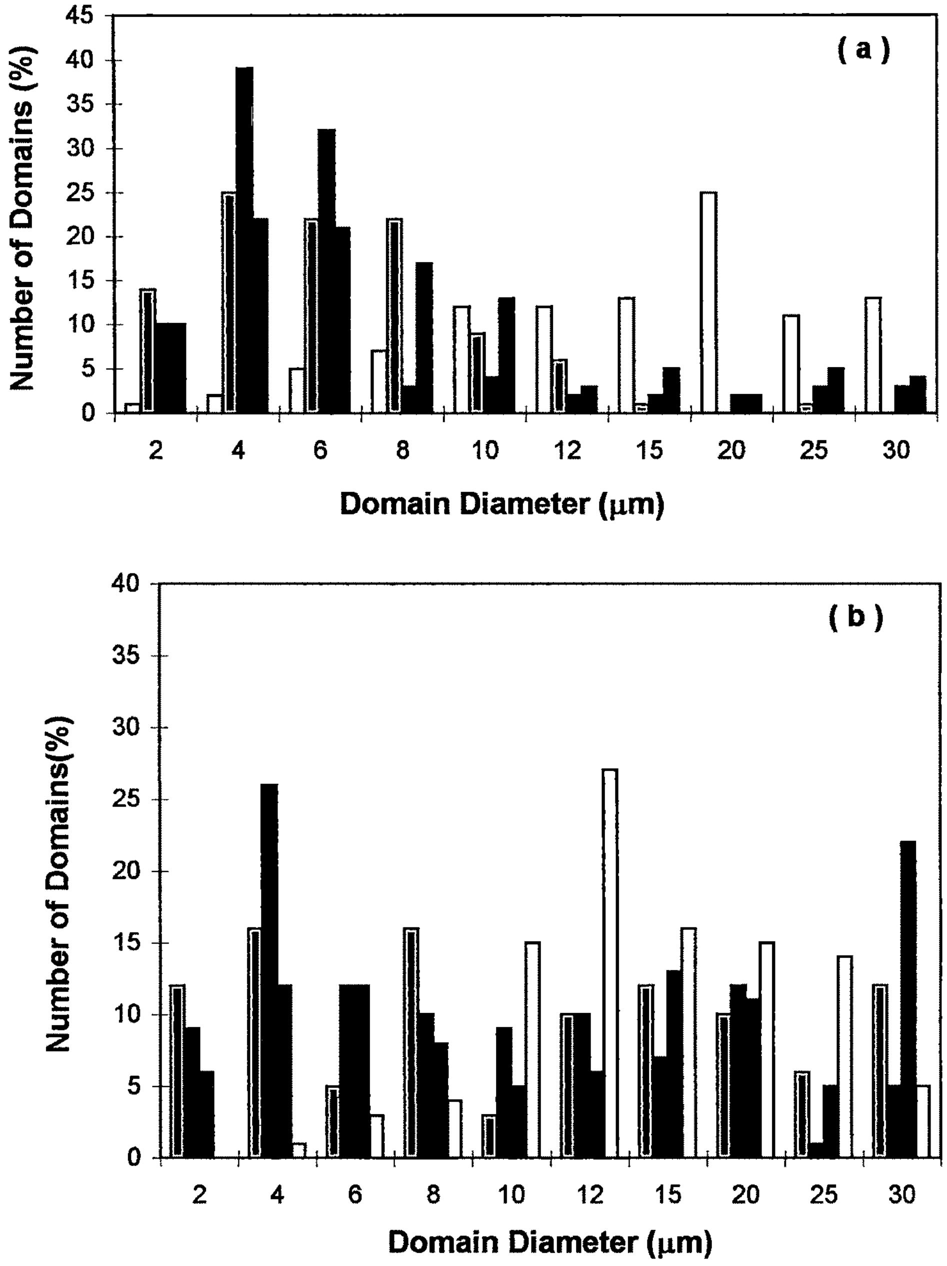


Fig. 3.4 Polydispersity of the Dispersed Phase in PP/ ABS /PP- g-acrylic acid

a: 85 / 15 / x , b: 75 / 25 / x

□ X = 0, ▣ X = 2.5, ■ X = 5, ■ X = 7.5

Mechanical Properties

Mathematical models

Many theories have been put forward for the prediction of elastic modulus of heterogeneous blends[115]. There are three principal groups of models that can predict the modulus - composition dependence of blends.

(i) Mechanical coupling model,
(ii) Self-consistent model, and
(iii) Bounds on modulus model

Among these self consistent model which is widely used for various blends is based on three assumptions,

(i) Perfect adhesion exists between the matrix and the inclusions
(ii) Interinclusion interactions are negligible and
(iii) The inclusions are spherical.

Based on these assumptions Kerner[116] proposed the following model for the systems having similar Poisson's ratio (υ) and perfect adhesion at boundary, for the calculation of tensile modulus (E) as

$$\mathbf{E_b = E_m \frac{\{ \varnothing_d E_d / [(7 - 5\, \upsilon_m) E_m + (8 - 10\upsilon_m) E_m] + \varnothing_m 15 (1- \upsilon_m)\}}{\{ \varnothing_d E_m / [(7 - 5\, \upsilon_m) E_m + (8 - 10\upsilon_m) E_d] + \varnothing_m 15 (1 - \upsilon_m)\}}} \qquad (4)$$

Where E is the tensile modulus $\varnothing$ is the volume fraction and υ is the Poisson's ratio. Subscripts b, m and d refer to the blend, matrix and dispersed phases respectively.

For the blends in which inclusions are loosely bound, they contribute a little to the overall modulus of blends (E_b). Hence, the observed modulus of blends is mainly due to the matrix and contribution of E_d is negligible ($E_d \cong 0$). As a result above equation is reduced to

$$\frac{1}{E_b} = \frac{1}{E_m}\left[1 + \frac{\varnothing_d 15(1 - \upsilon_m)}{(7 - 5\upsilon_m)\varnothing_m}\right] \qquad (5)$$

In Kerner's model only particle - matrix interaction, but no particle-particle interaction was considered. Therefore, Kerner's model was modified by Nielsen[117] by considering particle - particle interaction in blend. According to Nielsen

(1) for a rigid polymer, dispersed in rubber matrix

$$\frac{E_b}{E_m} = \frac{1 + A\,B\,\varnothing_d}{1 - B\,\psi\,\varnothing_d} \qquad (6)$$

where $B = (E_d / E_m - 1) / (E_d / E_m + A)$ and $\psi = 1 + (1 - \varnothing_{max} / \varnothing^2_{max})\varnothing_d$ and

(2) for a rubbery polymer ,dispersed in a rigid matrix

$$\frac{E_m}{E_b} = \frac{1 + A B_i \varnothing_d}{1 - B_i \psi\, \varnothing_d} \qquad (7)$$

where $B_i = E_m / (E_d - 1) / (E_m / E_d + A)$ and $\psi = 1 + (1 - \varnothing_{max} / \varnothing^2_{max})\varnothing_d$

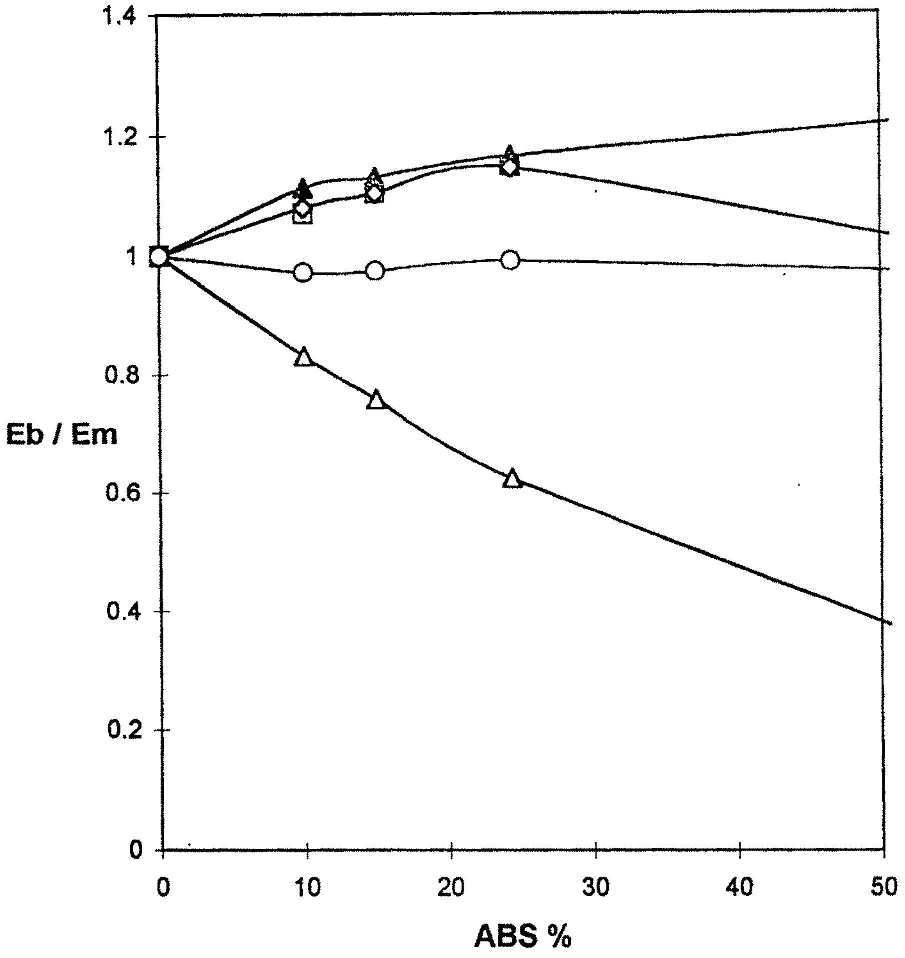


Fig. 3.5 Theoritical Models for the Tensile Modulus of PP / ABS Blends

Kerners' model for perfectively bound inclusions (▲)

Kerners' model for loosely bound inclusions (△)

Neilsens' model for rubber dispersed in rigid matrix (□)

PP / ABS blends experimental value (O)

PP / ABS /2.5% PP-g-acrylic acid blends' experimental value (◇)

TABLE 3.3 Adjusted $\varnothing_{max}$ values for PP /PP-g-acrylic acid / ABS

ABS w % in blends	$\varnothing_{max}$ for PP / PP-g-acrylic acid / ABS Blends			
	PP-g-acrylic acid 0 w%	PP-g-acrylic acid 2.5 w %	PP-g-acrylic acid 5 w%	PP-g-acrylic acid 7.5 w%
10	0.45	0.41	0.37	0.42
15	0.69	0.43	0.39	0.52
25	0.75	0.44	0.38	0.67
75	1.32	1.16	1.03	1.17
85	1.36	1.24	1.10	1.22
90	1.35	1.32	1.21	1.23

The constant A is $(7 - 5\upsilon_m) / (8 - 10\upsilon_m)$ for equation for rigid polymer dispersed in rubber matrix and $(8 - 10\upsilon_m) / (7 - 5\upsilon_m)$ for rubbery polymer dispersed in a rigid matrix. $\varnothing_{max}$ is the maximum packing volume and can be considered as a scale of interaction between two phases. A smaller value of $\varnothing_{max}$ represents a larger interface, and large value of $\varnothing_{max}$ represents smaller interface. Tensile modulus of the blends under study was calculated by using these models and considering Poission's ratio υ for PP and ABS as 0.35 and 0.39 respectively. The calculated tensile modulus values were compared with those obtained experimentally (**Figure 3.5**).

The values of $\varnothing_{max}$ are obtained by fitting the theoretical data with experimental data of binary as well as ternary blends using Nielsens' model (**Table 3.3**). The larger $\varnothing_{max}$ values were obtained for binary blends at all compositions as compared to the compatibilised blends which indicates the coarse particles formation in binary blends (**Fig.3.1.a, b**) whereas finer particles are obtained after compatibilization (**Fig.3.3.a-c**). The $\varnothing_{max}$ value increased with increase in ABS concentration, which indicates the large coarse particles formation even after addition of compatibilizer (**Table-3.2**).

Kerners' model for loosely bound dispersion shows considerable deviation of the experimental values for binary as well as ternary blends from theoretical values. Hence it can be assumed that some sort of adhesion/ interaction exits even in binary blends which may be due to higher coefficient of thermal expansion of PP as compared to ABS (1.7×10^{-4} k^{-1}

and 0.8 $\times 10^{-4}$ k^{-1} respectively for PP and ABS[118]). Hence PP contracts more than ABS upon cooling. Thus in PP rich blends ABS phase gets tightly embedded in PP matrix imparting increased tensile modulus even in binary blends. Application of Kerners' perfect adhesion model to the blends under study shows better agreement of the experimental data with the theoretical values. The observed positive deviation in compatibilised blends shows better adhesion between phases as compared to binary blends.

Addition of ABS to PP increases the tensile modulus of the blends as shown in **Figure 3.6.** From the results it can be observed that the tensile modulus of ternary blends is higher than that of binary blends. As per the expectations incorporation of ABS into PP increases the modulus due to the stiffening effect of ABS, which further increases upon addition of compatibiliser.

Tensile Properties

Typical stress-strain curves for PP, ABS and their binary (PP / ABS) and ternary (PP / ABS / PP-g-acrylic acid) blends are given in **Figure 3.7**. From the results it can be inferred that on addition of ABS the ductility of blends decreases even in ternary blends. The fracture of blends containing 10 – 20 % ABS was ductile in nature (**Fig.3.7**), whereas brittle fracture was observed when the concentration of ABS exceeded 25 w % in blends. This indicates poor adhesion between two phases at > 25 w % ABS in blends even after addition of compatibilizer. The decrease in

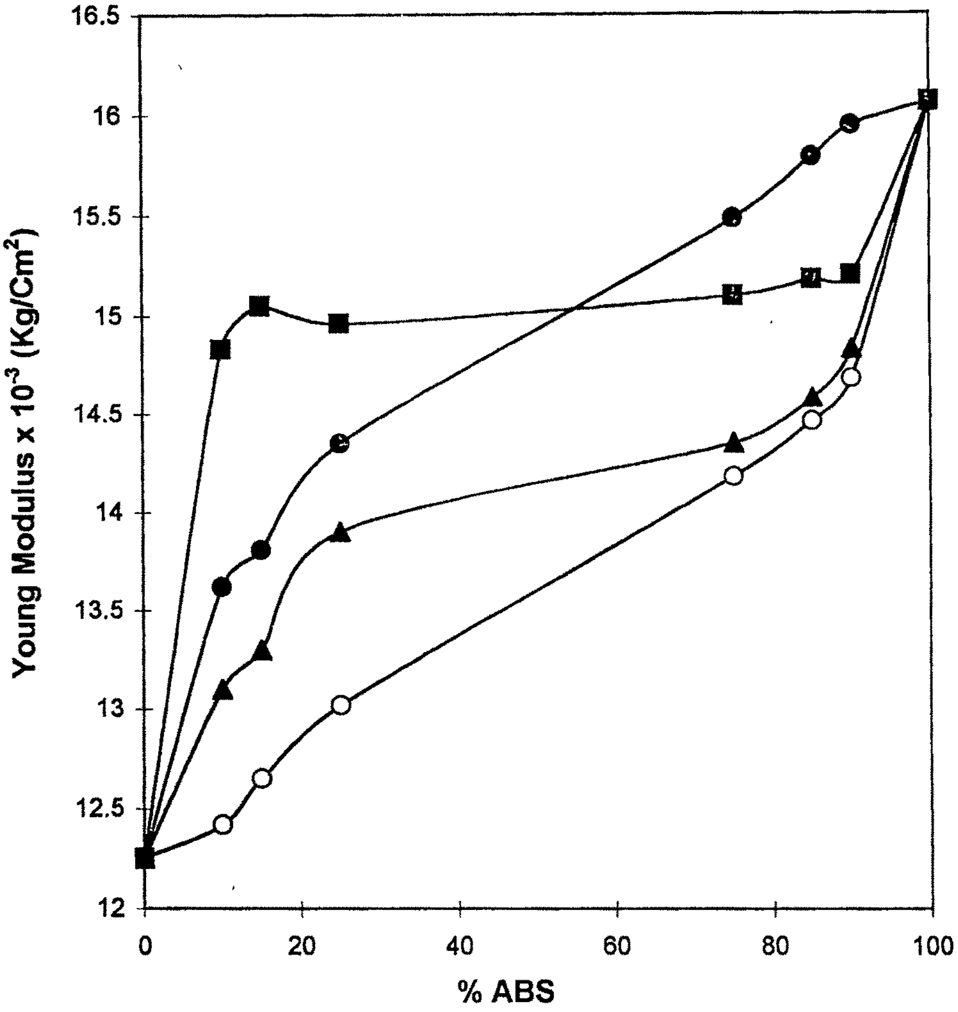


Fig. 3.6 Tensile Modulus of PP/ ABS Blends

PP/ ABS / PP-g-acrylic acid blends with

(O) 0 % , (●) 2.5 %, (■) 5 % and (▲) 7.5 % PP-g-acrylic acid

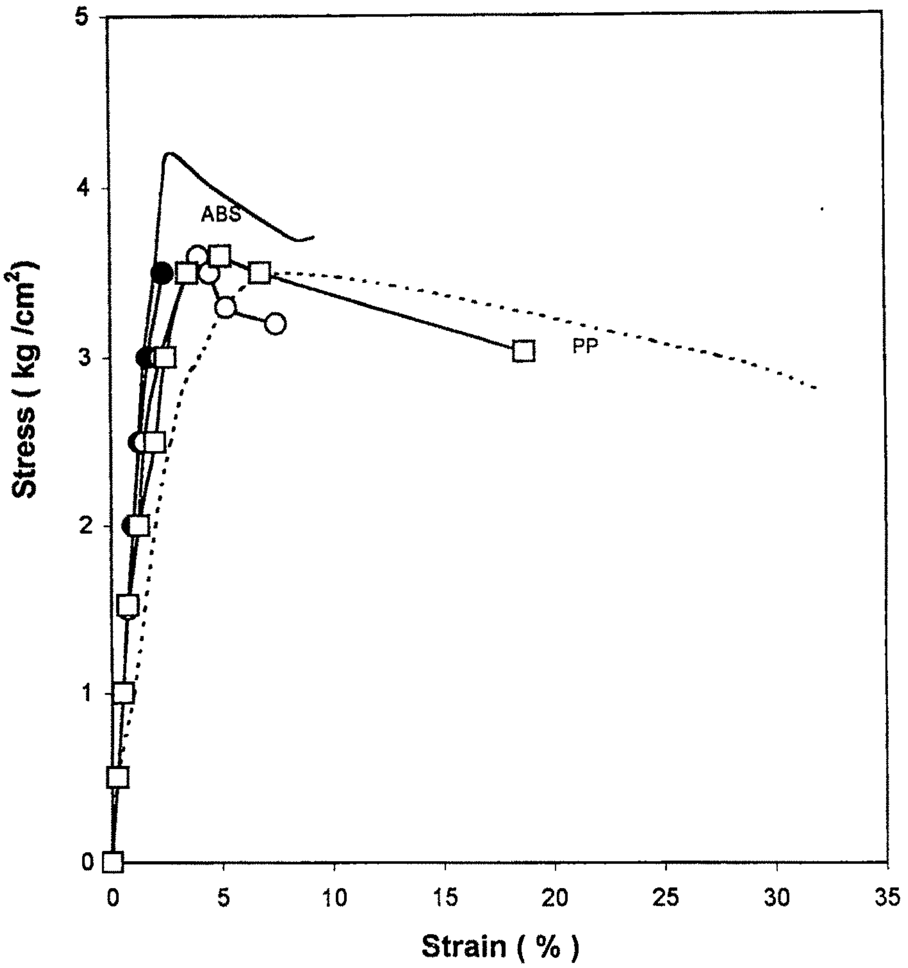


Fig. 3.7 Stress- Strain Curves for PP ABS Blends

(——) ABS; (- - - -) PP ;

(●) 75 / 25 / 2.5 PP / ABS / PP-g-acrylic acid;

(O) 85 / 10 / 2.5 PP / ABS / PP-g-acrylic acid;

(□) 90 / 10 / 2.5 PP / ABS / PP-g-acrylic acid crystallinity with increased ABS concentration is also responsible for the observed decrease in the elongation of blends.

Improvement in tensile strength on addition of compatibilizer was observed only in the blends rich in PP (**Fig.3.8**). Maximum tensile strength was observed for the blends containing 5 % compatibilizer. However, in ABS rich blends incorporation of PP drastically decreases the tensile strength of binary as well as ternary blends and hence ABS rich blends are not recommended.

Impact and Flexural Properties

Figure 3.9 illustrates the impact strength of PP / ABS and PP / ABS / PP-g-acrylic acid blends as a function of blend composition. As seen from **Figure 3.9**, only 5% compatibilizer is enough to improve the impact strength of blends significantly. Further increase in compatibilizer did not show improvement in impact strength. This can be attributed to the smaller particle size of the dispersed phase (**Fig.3.3**) in the blends containing 5 w % of the compatibilizer. Increase in particle size of dispersed phase allows the less dissipation of impact energy and thus it shows the high impact strength. Blends with 2.5 w % and 7.5 w % of compatibilizer concentration in blends show lower impact strength due to the larger particle size compared to 5 w % compatibilizer concentration. The sharp decrease in elongation was observed in binary as well as ternary blends with increasing concentration of ABS (**Fig.3.10**). Incorporation of ABS in PP decreases the elongation properties of PP. Due to increased adhesion at interface the flexural modulus increases when

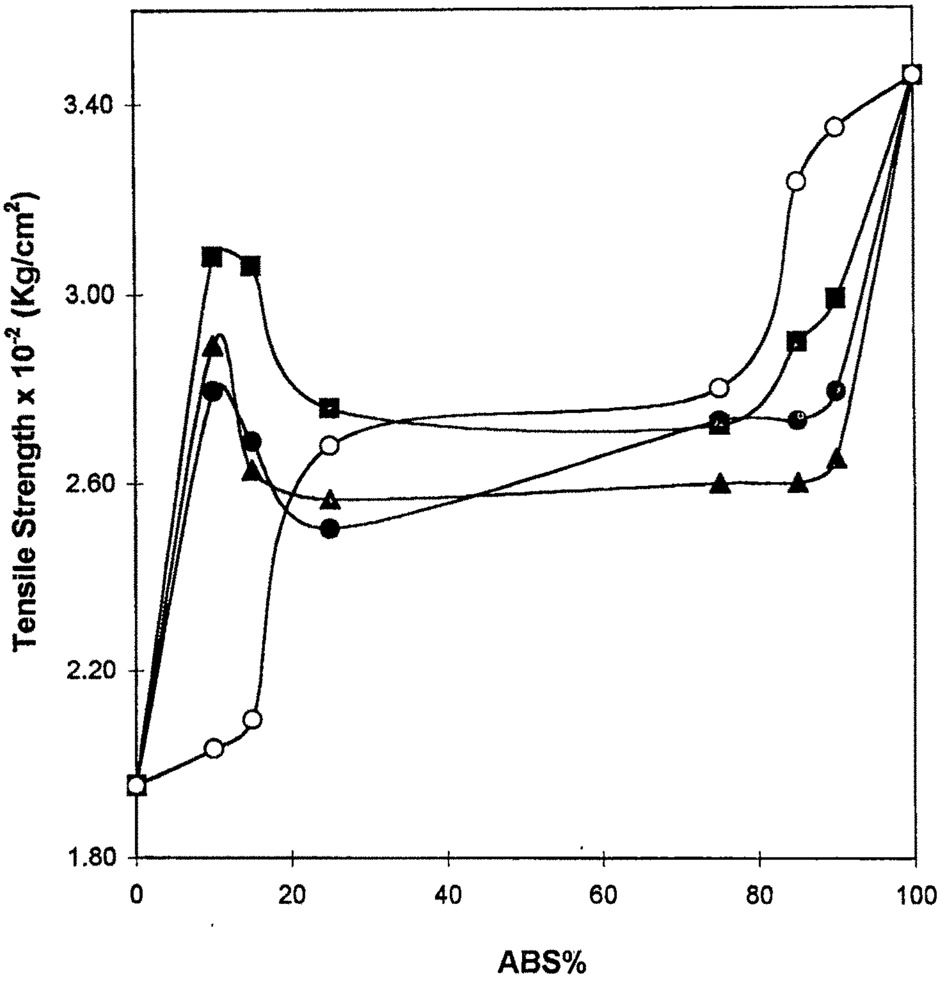


Fig. 3.8 Tensile Strength of PP / ABS Blends

PP/ ABS / PP-g-acrylic acid blends with
(O) 0 % , (●) 2.5 %, (■) 5 % and (▲) 7.5 %
PP-g-acrylic acid

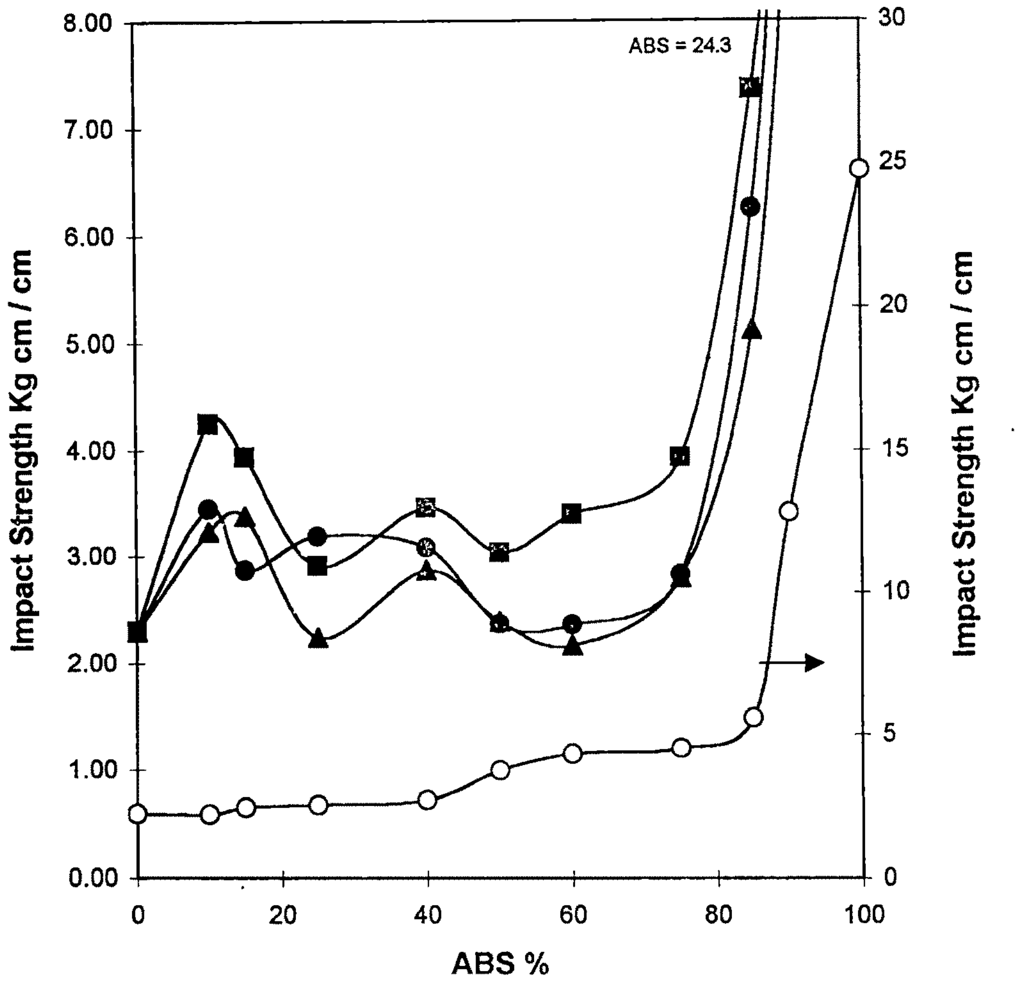


Fig. 3.9 Impact Strength of PP / ABS Blends

PP / ABS / PP-g-acrylic acid blends with

(O) 0 %, (●) 2.5 %, (▨) 5 % and (▲) 7.5 % PP-g-acrylic acid

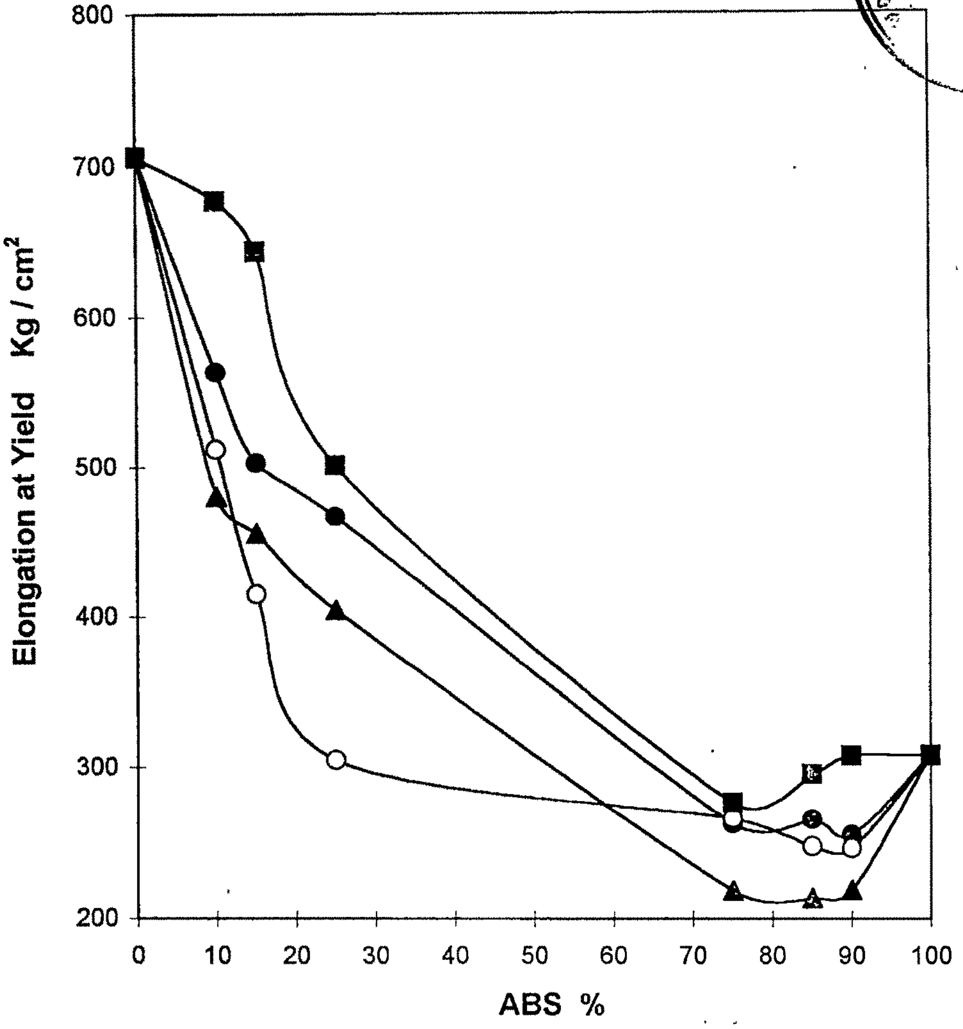


Fig. 3.10 Elongation at Yield of PP / ABS Blends

PP/ ABS / PP-g-acrylic acid blends with

(O) 0 % , (●) 2.5 %, (■) 5 % and (▲) 7.5 % PP-g-acrylic acid

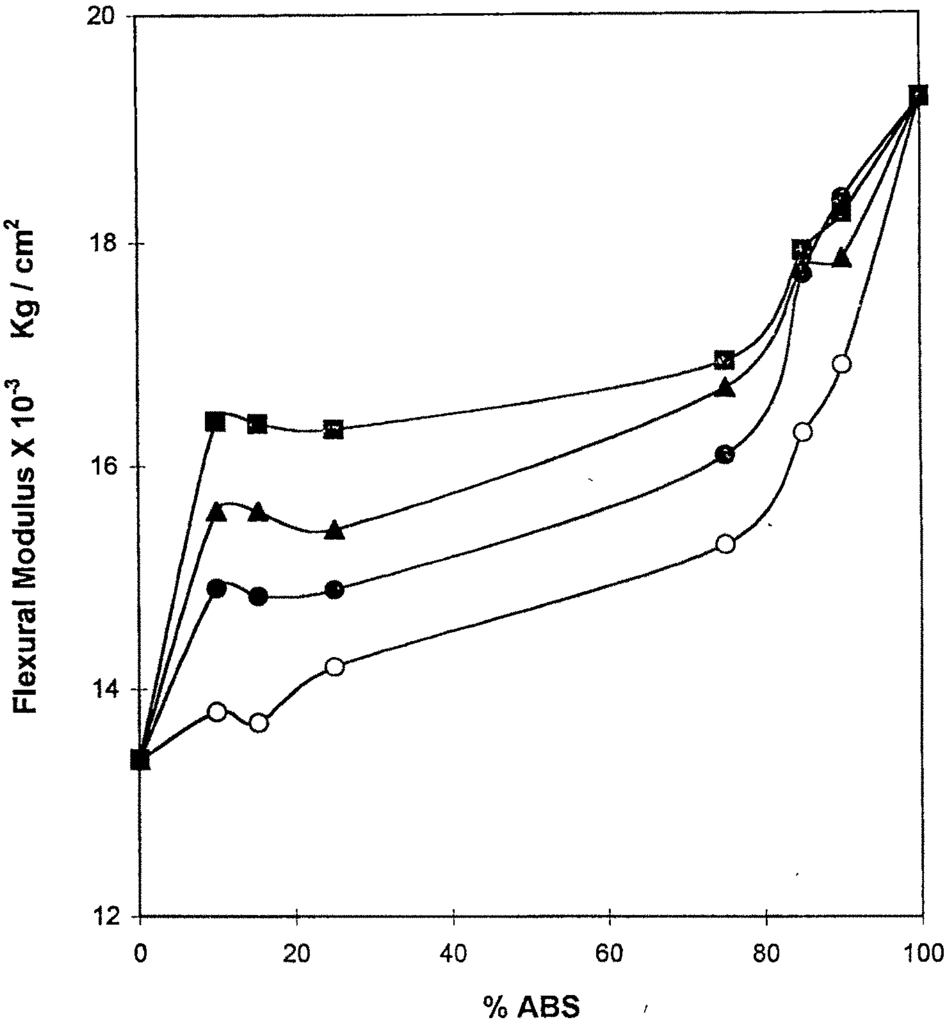


Fig. 3.11 Flexural Strength of PP / ABS Blends

PP/ABS / PP-g-acrylic acid blends with

(O) 0 % , (●) 2.5 %, (■) 5 % and (▲) 7.5 % PP-g-acrylic acid

PP / ABS blends were compatibilized. The Addition of 5 w% compatibiliser gave maximum flexural modulus for the blends containing 10 - 15 w % of ABS (**Fig.3.11**).

[illegible]

- PP-g-acrylic acid is effective compatibiliser for PP/ ABS blends
- The 5 % of compatibiliser PP-g-acrylic acid in PP rich blends gives maximum impact strength, modulus and tensile strength
- All the compatibilized blends have higher modulus compared to uncompatibilized blends
- PP rich blends are ductile in nature and ABS rich blends are brittle in nature irrespective to compatibilization.
- Compatibilization upto 5% leads to finer dispersion of ABS in PP

3.7.2 Compatibilization of PP/ABS blends by using PP-g-2-HEMA

The compositions of binary and ternary blends of PP / ABS and PP / PP-g-2-HEMA / ABS are given in **Table-3.1.** Fowler et. al.[119] and Lee et. al.[120] in their studies of PMMA / ABS and MMA-GMA copolymer / ABS blends reported better miscibility of ABS with PMMA and MMA-GMA copolymers. The miscibility of blend is attributed to the miscibility of styrene-acrylonitrile part of ABS and acrylate groups of MMA and GMA units. In the present study compatibilization of PP/ABS blends using PP-g-2-HEMA is under taken. The blends were studied for morphological and mechanical properties

Morphology

Scanning Electron Micrographs (SEM) of room temperature fractured PP / ABS binary blends did not show any adhesion at the interface of PP – ABS (**Fig. 3.12 a, b**). The observed smoother surfaces of the cavities in binary blends indicate no adhesion between the inclusions and matrix. As a result inspite of smaller and homogeneous dispersion of ABS in PP the blends showed incompatibility. In the blends containing 10 w % of ABS, the particle size was observed to be 10 -15 μm whereas in the blends containing 15 w % of ABS it was 20 - 30 μm (**Fig.3.12.a, b, Fig.3.13 and Fig.3.14**). Thus the size of the dispersed phase in the blends was observed to increase with increasing concentration of dispersed phase. On the addition of compatibiliser marked difference was observed in the

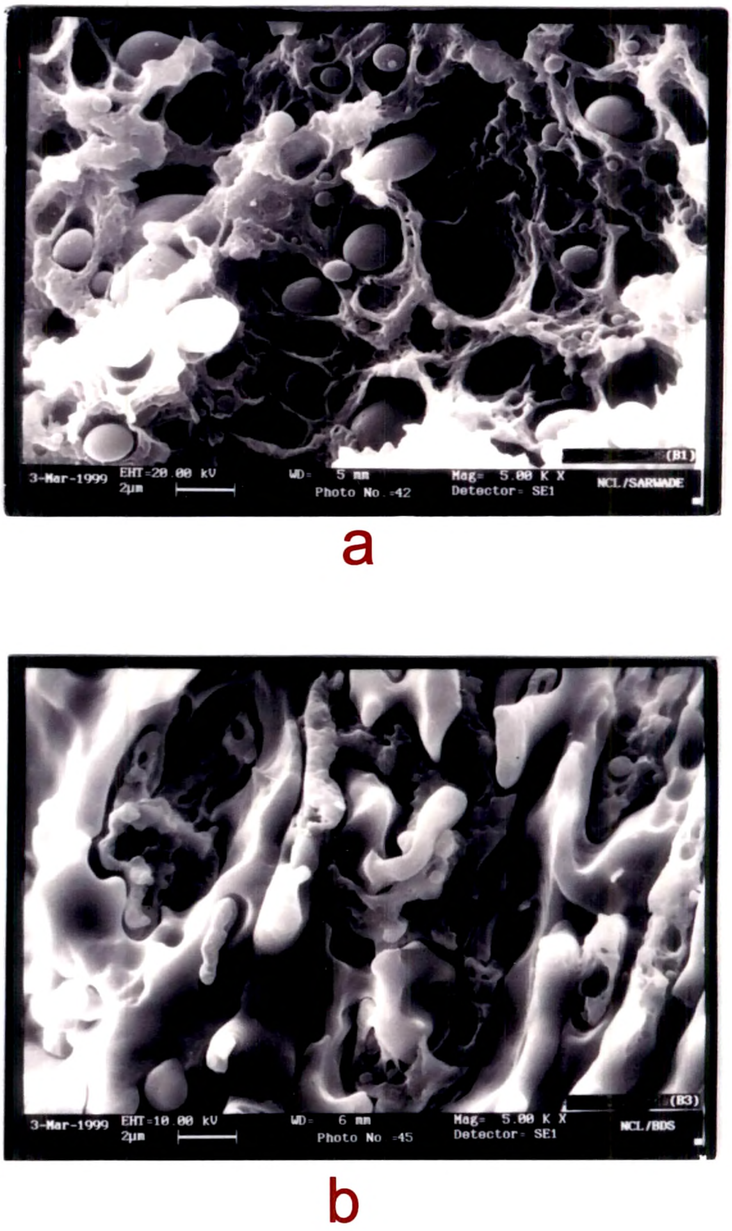


Fig.3.12 SE micrographs of impact fractured surfaces of PP/ ABS blends

a : 90 / 10 , PP / ABS ; **b : 85 / 15 ,** PP / ABS

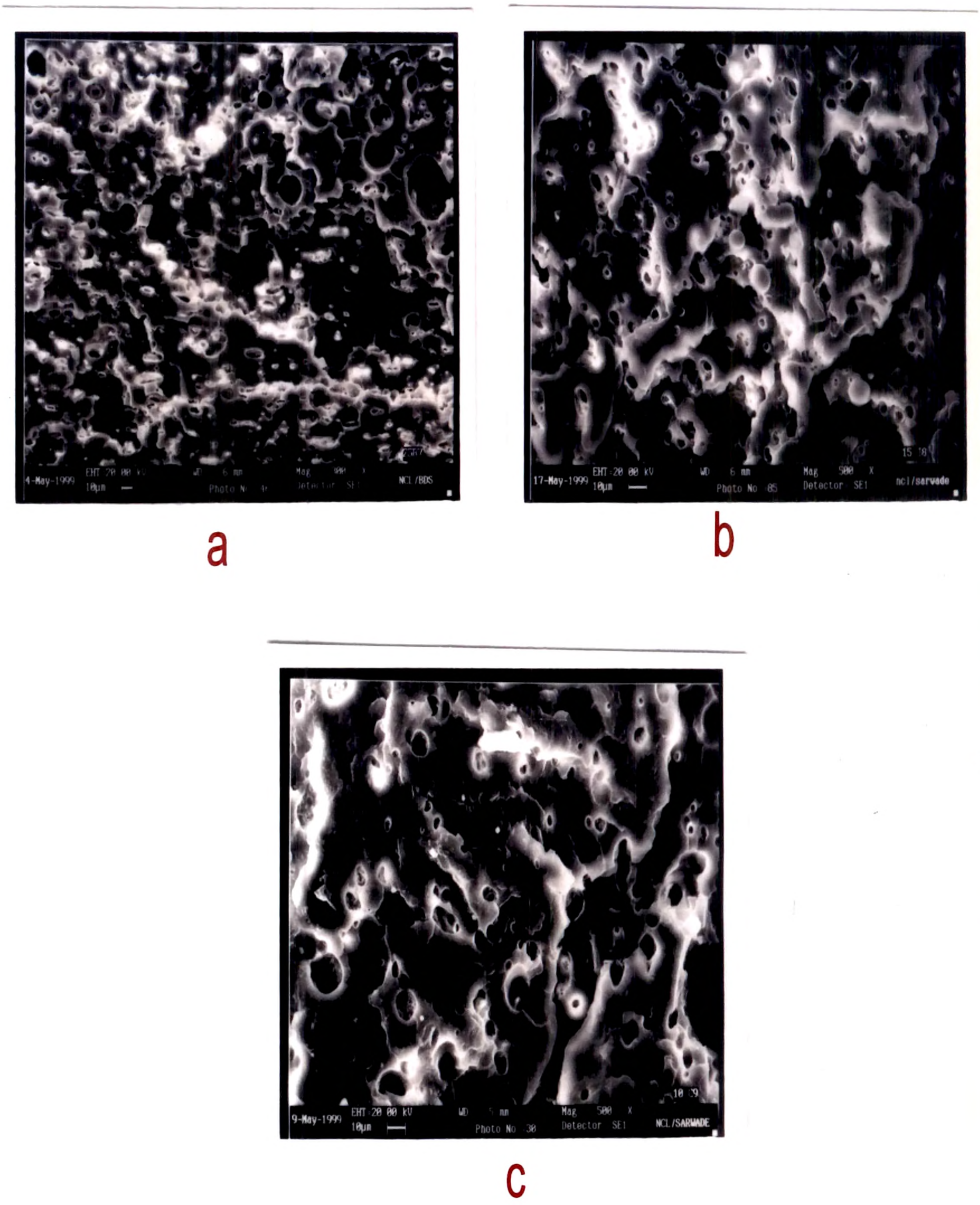


Fig. 3.13 SE micrographs of impact fractured surfaces of PP/ ABS / PP-g-2-HEMA blends after extraction of ABS in MEK

a : 75 / 25 /2.5; **b** : 75 / 25 /5 ; **c** : 75 / 25 / 7.5

morphology of binary blends. Addition of 2.5 w % of PP-g-2-HEMA to PP / ABS binary blends increased the adhesion between phases and decreased the size of dispersed phase to 5 - 10 μm (**Fig.3.13**). The dispersion was observed to be more homogeneous and finer. The rough surface of the cavities formed due to the etching of dispersed phase also indicates existence of adhesion at interface (**Fig.13 a-c**).

From the SEM the number average diameter $D\overline{n}$, weight average diameter $D\overline{w}$ and surface area average diameter $D\overline{vs}$ were calculated and were used for the determination of polydispersity index PDI as discussed earlier. The results are given in **Table-3.4.**The polydispersity plots of the blends containing 85 and 75 % PP and different concentrations of compatibilizer are given in **Figure-3.14**. The uncompatibilized binary blends show the broader particle size distribution of ABS into PP. With incorporation of compatibilizer, the distribution of particle size becomes narrow and the size of the dispersed ABS particles also decreases.

Mechanical Properties

Stress-strain curves for binary PP / ABS and ternary PP / PP-g-2-HEMA / ABS blends are illustrated in **Figure 3.15**. It was observed that PP rich blends show ductile behaviour whereas blends with higher % of ABS (>15 w %) break before yield point indicating brittle behaviour.

Due to lower tensile modulus of PP the tensile modulus of all binary and ternary blends was observed to be lower than that of ABS (**Fig.3.16**). However, incorporation of PP in ABS does not show considerable effect on

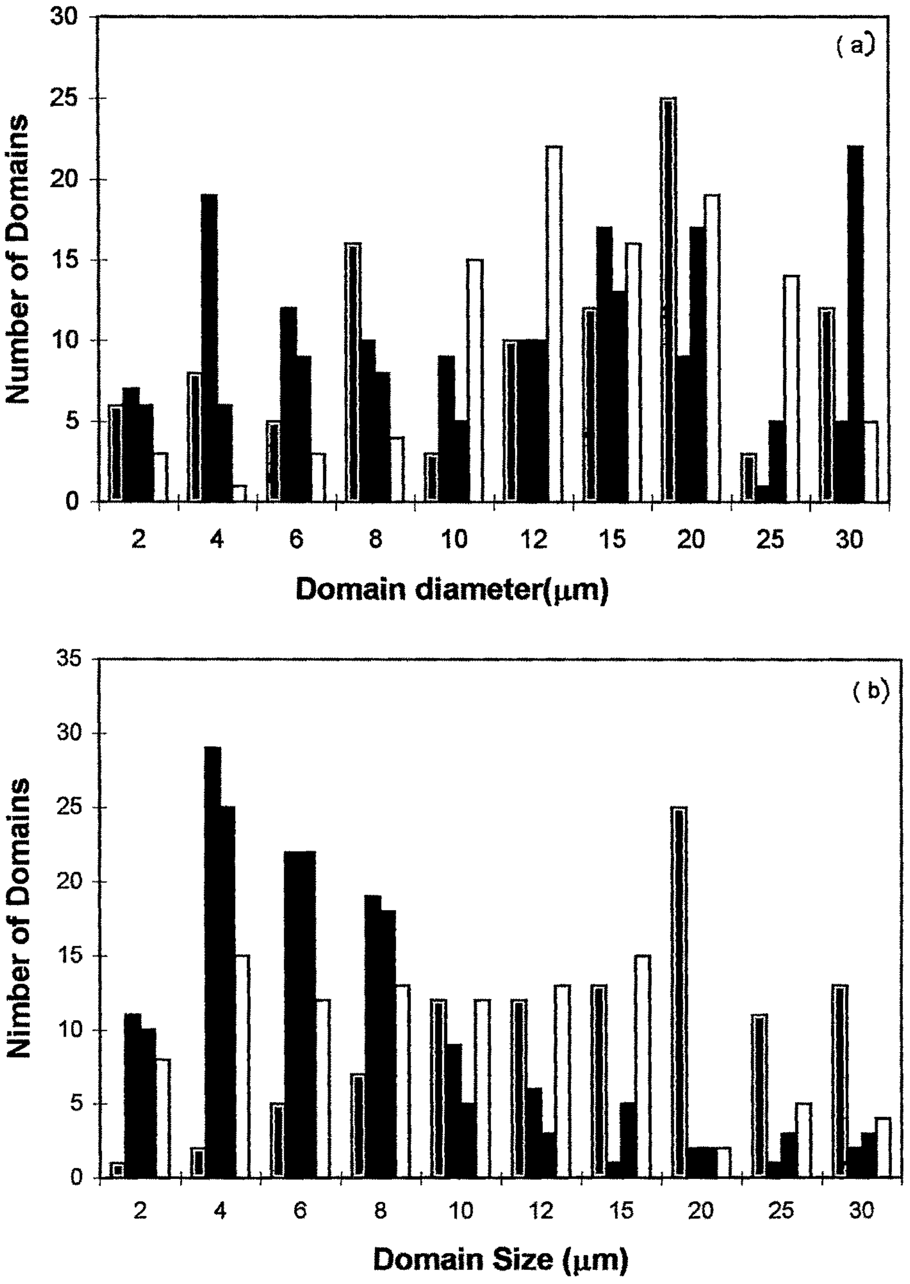


Fig. 3. 14 Polydispersity of the Dispersed Phase in PP/ ABS / PP-g- 2-HEMA

a: 75 / 15 / x , b: 85 / 25 / x

□ X = 0, ■ X = 2.5, ■ X = 5 , ■ X = 7.5

TABLE 3.4 Particle size and polydispersity index in blends

PP/ABS/ PP-g-2-HEMA	$\overline{Dn}$ (μm)	$\overline{Dw}$ (μm)	$\overline{Dvs}$ (μm)	PDI
90/10/0	7.50	8.33	11.0	1.11
90/10/2.5	4.26	4.81	6.59	1.12
90/10/5	4.1	4.43	6.96	1.08
90/10/7.5	5.15	6.32	7.23	1.22
75/25/0	6.9	8.12	10.12	1.31
75/25/2.5	5.12	5.83	7.15	1.13
75/25/5	5.45	6.19	9.12	1.13
75/25/7.5	6.11	7.85	9.65	1.28

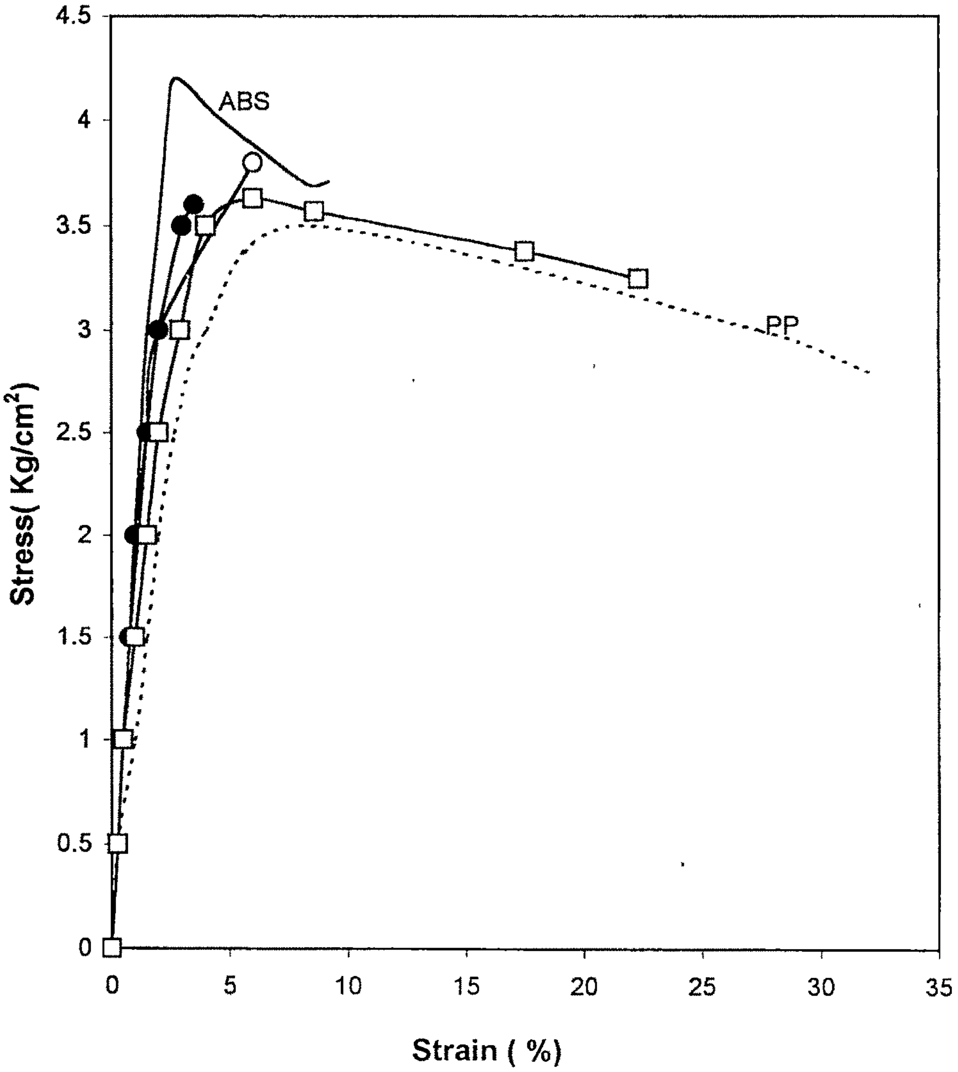


Fig. 3.15 Stress- Strain Curves for PP ABS Blends

—— ABS; - - - -PP ;

● 75 / 25 / 2.5 PP / ABS / PP-g-2-HEMA;

○ 85 / 15 / 2.5 PP / ABS / PP-g-2-HEMA ;

□ 90 / 10 / 2.5 PP / ABS / PP-g-2-HEMA

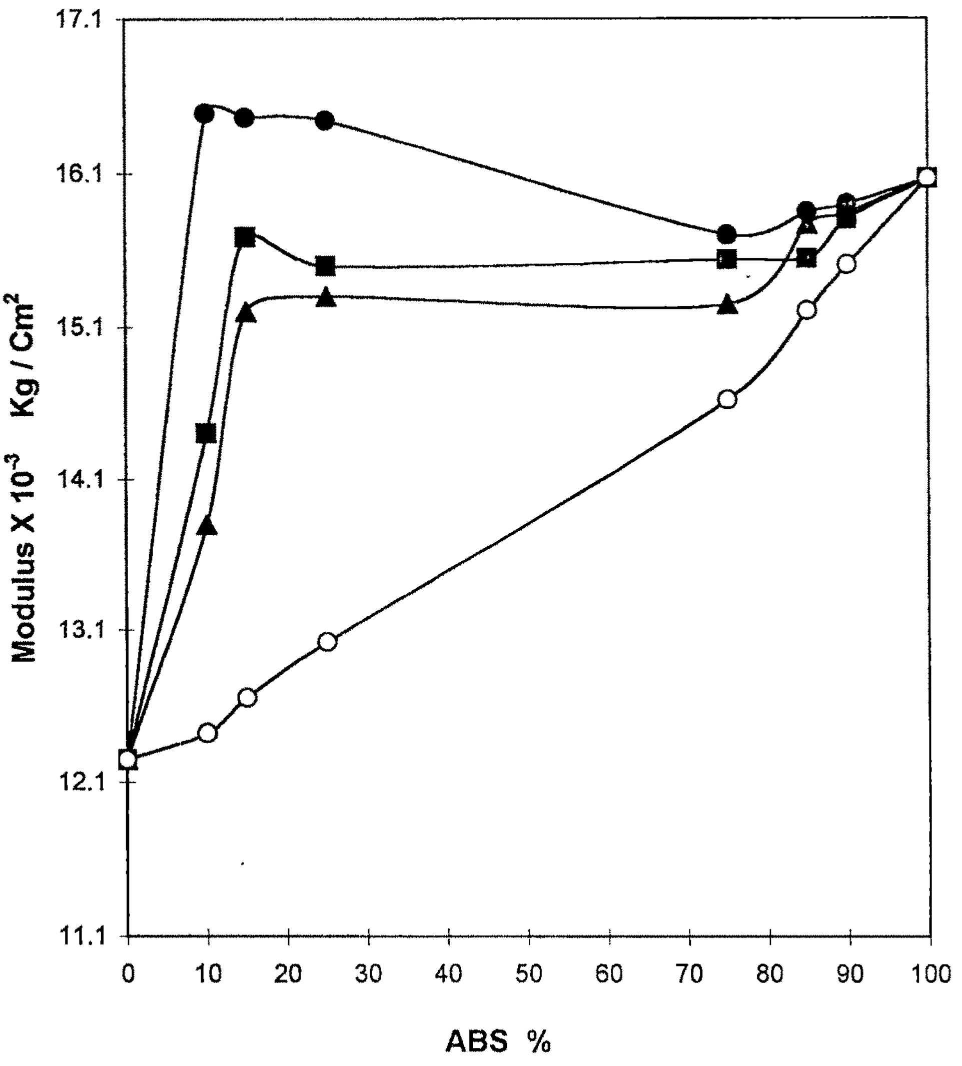


Fig. 3.16 Tensile Modulus of PP/ ABS Blends

PP/ABS / PP-g-2-HEMA blends with
(O) 0 % , (●) 2.5 %, (■) 5 % and (▲) 7.5 %
PP-g-2-HEMA

modulus but incorporation of ABS in PP shows considerable increase in the modulus of ternary blends. The tensile modulus of ternary blends was observed to be higher than that of binary blends at all compositions. This may be due to the finer and homogeneous dispersion and increased adhesion at the interface. Only 2.5 % of compatibiliser was observed to be sufficient to increase the tensile modulus to 1.5 folds. Further increase in compatibiliser concentration decreased the modulus value. The various mathematical models described in earlier section were used for the prediction of tensile modulus of the binary and ternary blends.

To see the validity of the mathematical models described earlier in **section 3.7.1** for the systems under examination, tensile modulus of the blends under study was calculated by using these models. The calculated tensile modulus values obtained through model were compared with those obtained experimentally (**Fig. 3.17**). It was observed that Kerner's model for loosely bound inclusion shows considerable deviation from the experimentally obtained data for binary as well as ternary blends. Hence it can be assumed that some sort of adhesion / interaction exists even in binary blends. This may be originating from the stiffening effect, which is attributed for higher coefficient of thermal expansion of PP as compared to ABS[118]. As a result upon solidification of blends PP phase contracts more than the dispersed ABS resulting into tightly embedded ABS in PP matrix imparting increased tensile modulus even in binary blends. However, this effect was observed more when compatibilizer was used. In addition to the stiffening effect, the factor further responsible for higher tensile modulus in compatibilized blends is increased homogeneity and

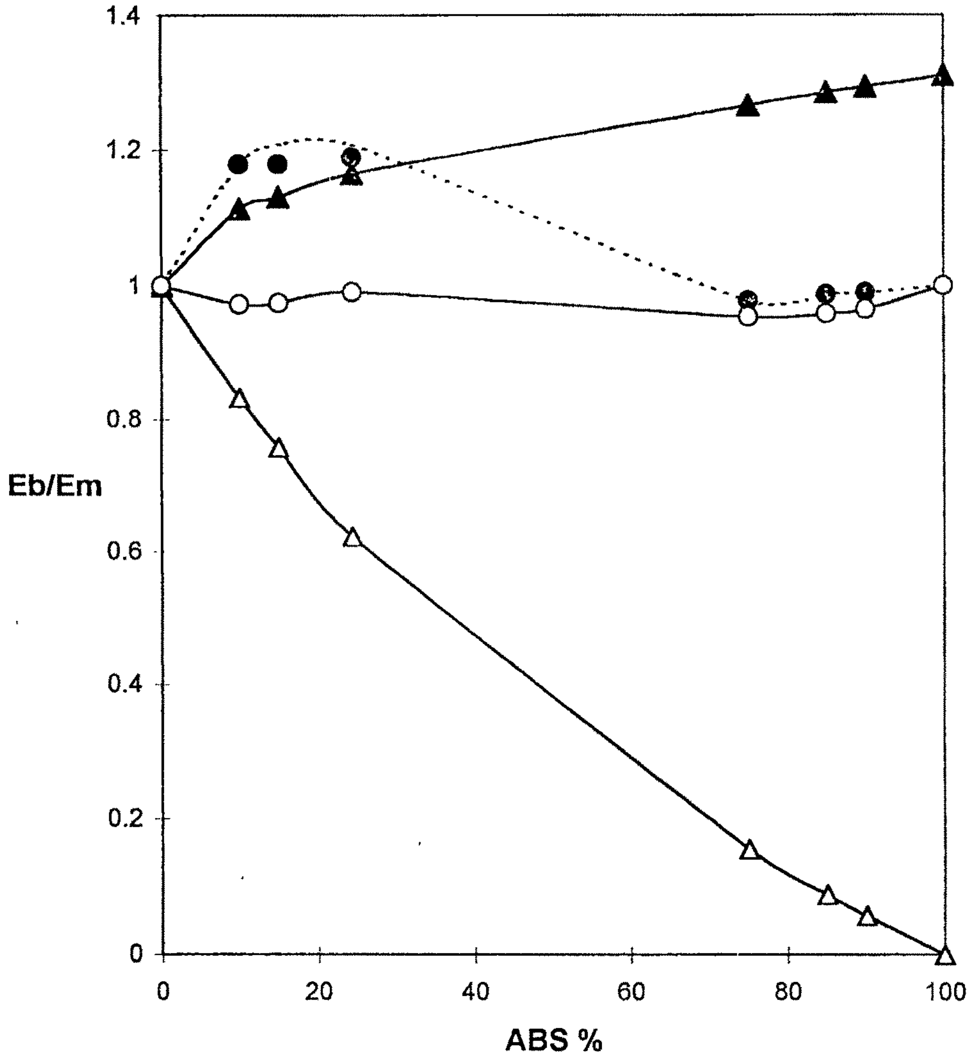


Fig. 3.17 Theoritical Models for the Tensile Modulus of PP / ABS Blends

Kerners' model for perfectively bound inclusions (▲)

Kerners' model for loosely bound inclusions (Δ)

Neilsens' model for rubber dispersed in rigid matrix (----)

PP / ABS blends experimental value (O)

PP / ABS /2.5% PP-g-2-HEMA blends experimental value (●)

finer dispersion observed in ternary blends. PP rich ternary blends showed more resemblances to the Kerners' model for perfectly bound inclusions.

Neilsen's model[117] predicts tensile modulus on the basis of $\varnothing_{max}$ values. The $\varnothing_{max}$ values were adjusted in such a way that the theoretically calculated modulus data matches with the experimentally obtained one. The $\varnothing_{max}$ values calculated for adjusting the theoretical values of tensile modulus with experimental data are given in **Table-3.5**. The larger $\varnothing_{max}$ values were obtained for binary blends at all compositions as compared to the compatibilised blends which indicates the coarse particles formation in binary blends (**Fig.3.1.a, b**) whereas finer particles are obtained after compatibilization (**Fig.3.13.a-c**). It was observed that with increased content of ABS, $\varnothing_{max}$ values go on increasing, indicating decrease in the volume of the interface, which is immobilised by the discrete phase in the blend. The reciprocal of $\varnothing_{max}$ can be considered as an interaction parameter, which is proportional to $(R+\Delta R)^3$, where R is the radius of the inclusion and ΔR is the depth of interface that is immobilised by the inclusion. For the given value of ΔR, the smaller the size of the inclusion, the smaller the $\varnothing_{max}$ value. It was observed that with increasing ABS content in blends, the dispersed particle size increases which supports the observed increase in the $\varnothing_{max}$ values (**Table-3.5**).

Tensile Properties

Flexural modulus and tensile strength were observed to increase with increased concentration of ABS in blends. The toughening effect of ABS increases the flexural modulus of the blends (**Fig.3.18**). The tensile

TABLE 3.5 Adjusted $\varnothing_{max}$ values for PP/ PP-g-2-HEMA / ABS blends

ABS w % in blends	$\varnothing_{max}$ for PP / PP-g- 2-HEMA / ABS Blends			
	PP-g-2-HEMA 0 w%	PP-g-2-HEMA 2.5 w %	PP-g-2-HEMA 5 w%	PP-g-2-HEMA 7.5 w%
10	0.35	0.34	0.41	0.48
15	0.42	0.43	0.49	0.52
25	0.54	0.63	0.64	0.67
75	1.32	1.16	1.03	1.17
85	1.36	1.24	1.14	1.20
90	1.35	1.31	1.22	1.23

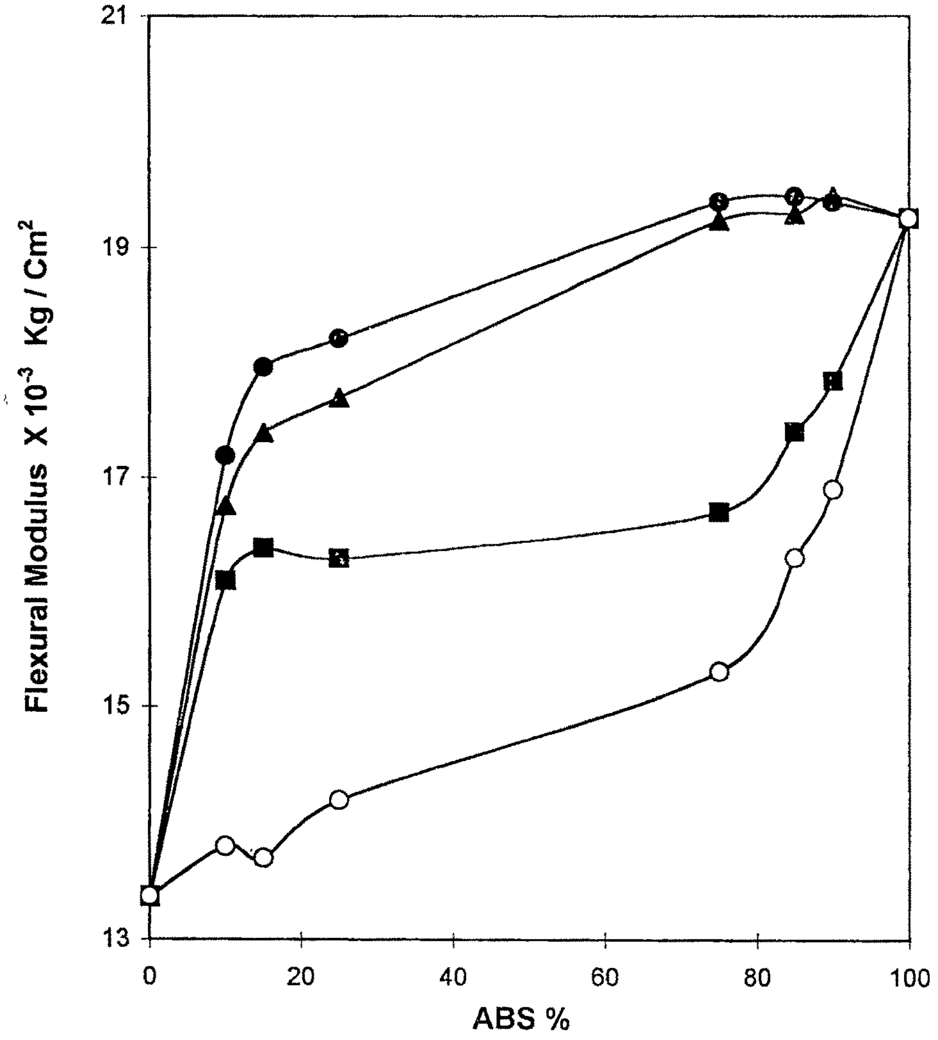


Fig. 3.18 Flexural Strength of PP / ABS Blends

PP/ABS / PP-g-2-HEMA blends with

(O) 0 %; (●) 2.5 %, (■) 5 % and (▲) 7.5 % PP-g-2-HEMA strength was also observed to increase with increased concentration of ABS in blends. Due to increase in adhesion at interface tensile strength of the ternary blends was observed to be higher compared to binary blends (**Fig.3.19**).

Sharp decrease in % elongation at break was observed in binary as well as ternary blends with incorporation of ABS into PP. However, decrease in % elongation was more critical in binary blends. It was observed that when ABS was incorporated in PP the elongation properties of blends decreased. This may be due to the plastication effect of the PP on ABS incorporation. (**Fig.3.20**).

Impact Properties

Figure3.21 illustrates the impact strength of PP/ABS binary and PP / PP-g-2-HEMA / ABS ternary blends as a function of ABS content in blends. As seen from **Fig.3.21**, 2.5 w % compatibilizer is sufficient for toughening the blends. Whereas, further incorporation of compatibilizer in blend does not show improvement in impact strength but rather decreases the impact strength. This can be explained from the observed smaller particle size of the dispersed phase at 2.5% compatibilizer concentration (**Fig.3.13**). The decrease in impact strength of blends with increased % of compatibilizer can be attributed to the formation of aggregates of compatibilizer in the bulk phase after a critical concentration of compatibilizer.

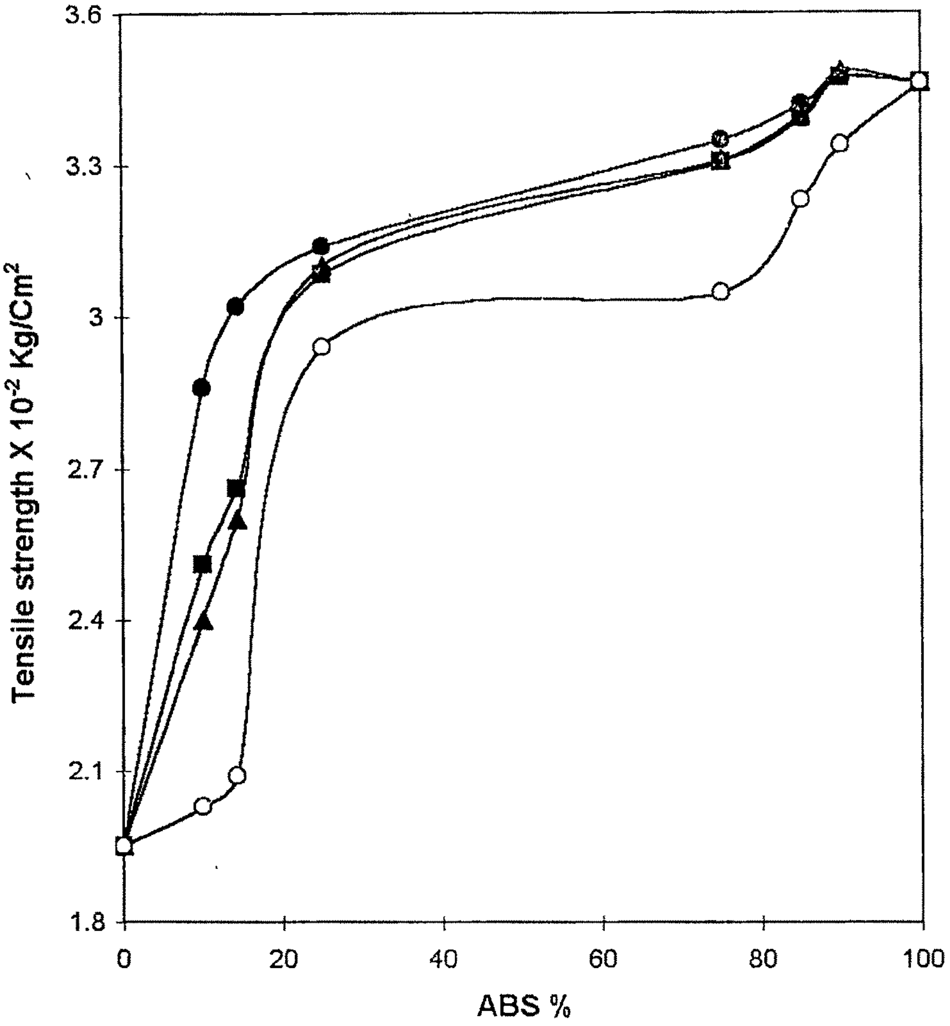


Fig. 3.19 Tensile Strength of PP / ABS Blends

PP/ ABS / PP-g-2-HEMA blends with

(O) 0 %, (●) 2.5 %, (■) 5 % and (▲) 7.5 % PP-g-2HEMA

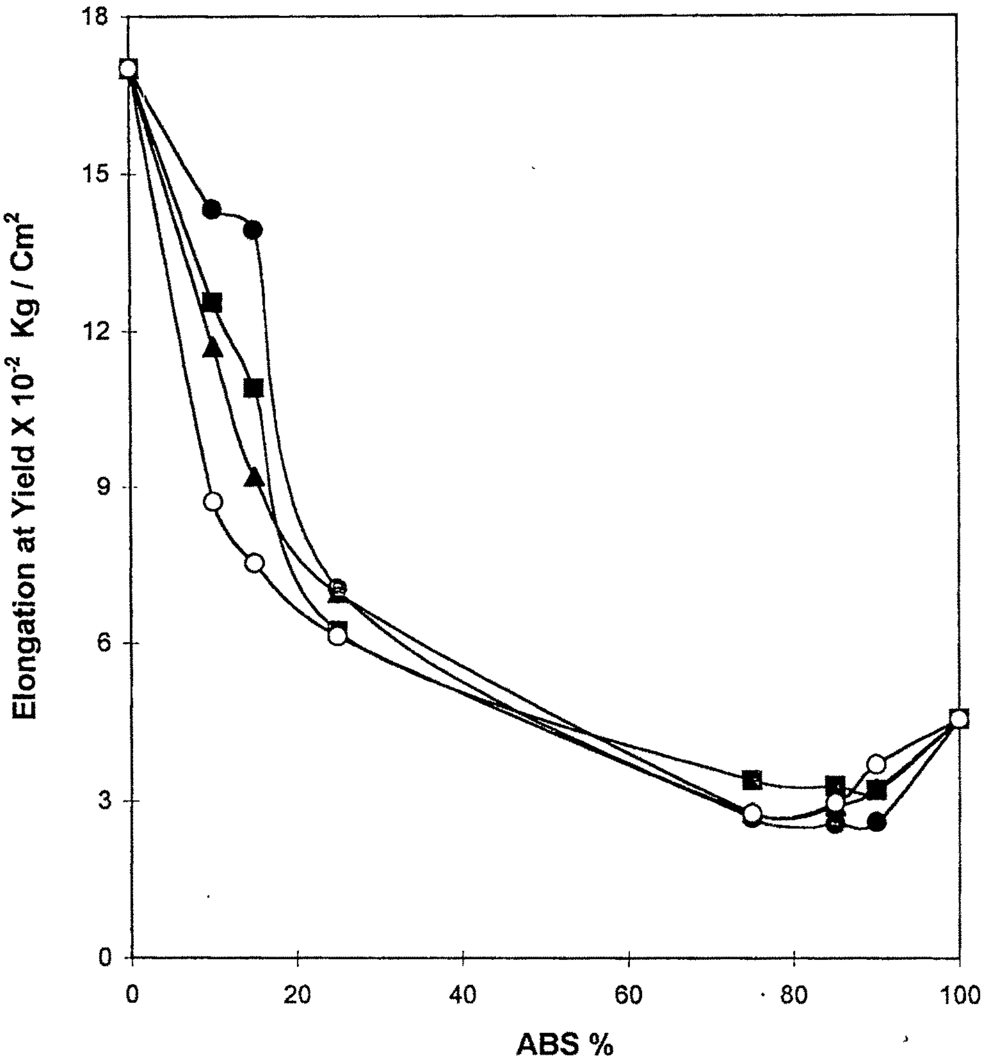


Fig. 3.20 Elongation at Yield of PP / ABS Blends

PP/ABS / PP-g-2-HEMA blends with

(O) 0 %; (⊛) 2.5 %, (■) 5 % and (▲) 7.5 %
PP-g-2-HEMA

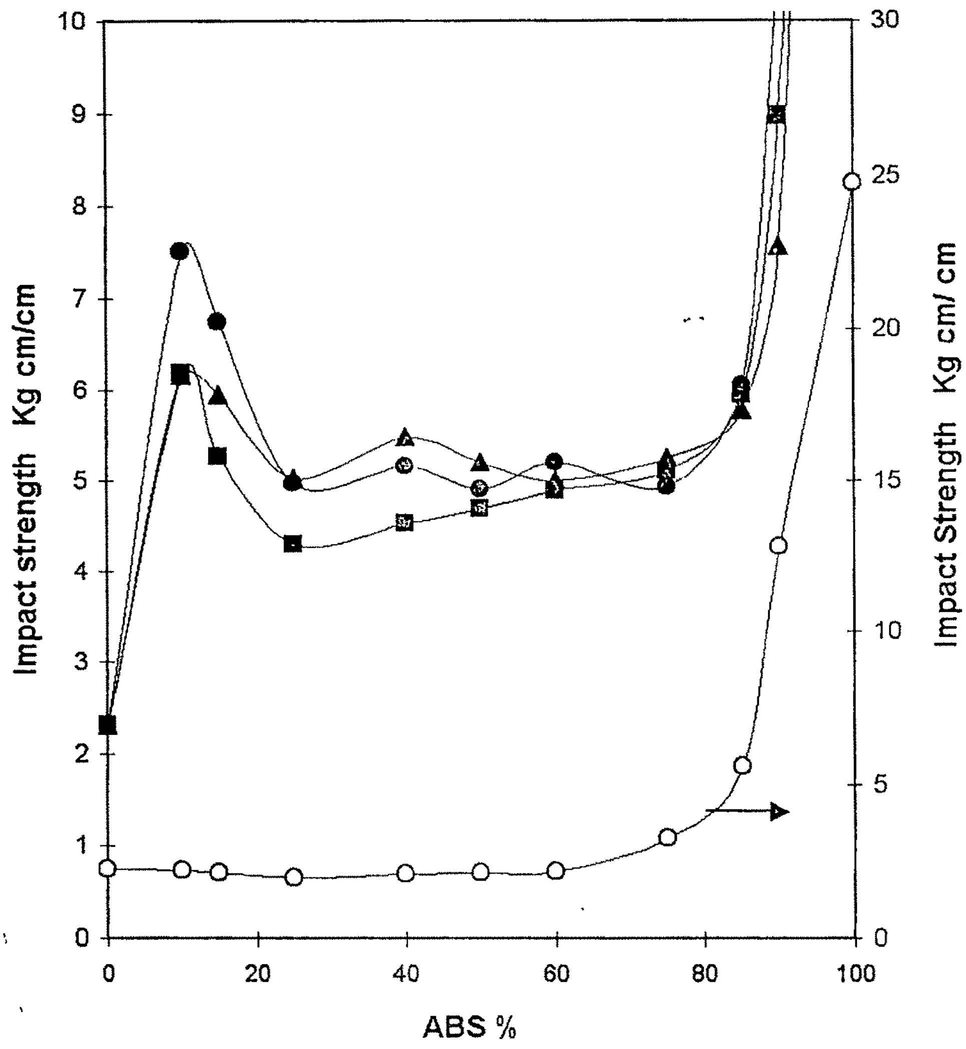


Fig. 3.21 Impact Strength of PP / ABS/ Blends

PP/ABS / PP-g-2-HEMA blends with

0 % (O), 2.5 % (●) , 5 % (■) , 7.5 % (▲)
PP-g-2-HEMA

[illegible]

- PP-g-2-HEMA is an effective compatibilizer for PP / ABS blends
- 2.5 % of PP-g-2-HEMA in blends give maximum impact strength and modulus
- PP rich blends are ductile in nature whereas ABS rich blends are brittle in nature irrespective of compatibilization
- PP/ ABS blends have poor elongation but have higher flexural modulus as compared to PP and ABS

3.7.3 Compatibilisation of PP/ABS blends by using PP-g-St-AN

Homogeneity of polymer blends depends on the mutual solubility of the polymeric components. However, most of the polymer pairs tend to be immiscible due to the difference in viscoelastic properties, surface tension, and intermolecular interactions. To reduce surface tension and to increase molecular interactions, a third component known as compatibilizer is used[15].

In the previous works PP-g-acrylic acid and PP-g-2-HEMA were used as compatibilizers in PP/ABS blends. In this work PP-g-St-AN was used for compatibilization of PP / ABS blends[121]. The objective of this work is to use PP-g-St-AN graft copolymer as a compatibilizer for PP / ABS blends, which contain St-AN, which is also a main constituent of ABS tercopolymer. Thus this graft copolymer can show a better compatibility in PP / ABS blends. The compositions of binary and ternary blends of PP / ABS and PP / PP-g-St-AN / ABS are given in **Table-3.1**.

Morphology

Scanning electron micrographs of room temperature fractured PP / ABS binary blends as shown in **Fig. 3.12 a, b** did not show any adhesion at interface .The smoother surfaces of the cavities observed in binary blends indicate no adhesion between inclusions and matrix. This indicates incompatibility of the phases inspite of the finer and homogeneous dispersion of ABS in PP matrix. Compatibilization of PP/ABS by the use of

PP-g-acrylic acid and PP-g-2-HEMA resulted into well dispersed and well distributed particles of dispersed ABS phase. Which were easily extractable with MEK. However, in the blends compatibilized with PP-g-St-AN extraction of ABS phase was not possible due to increased adhesion between the matrix and the inclusions. The SE micrographs of PP/ABS /PP-g-St-AN blends are shown in **Fig. 3.22 (a-c)**. Compatibilization of PP/ ABS blends by PP-g-St-AN resulted into finer and spherical particles of dispersed ABS phase. Surprisingly the cavities were not formed after extraction of ABS, which is unusual. It can be seen that the particles are spherical in shape with $< 1\mu m$ size.

From SE micrographs it can be observed that at 2.5 w % of compatibilizer dispersed particles are of smaller size whereas at 5 % compatibiliser concentration particle size was observed to increase and at 7.5 % compatibiliser concentration particles formed aggregates with threadlike structure (**Fig.3. 22.a-c**). The dispersion was observed to be more homogeneous and finer than in the case of blends compatibilised with PP-g-2-HEMA and PP-g-acrylic acid.

Mechanical Properties

Stress-strain curves for binary PP / ABS and ternary PP / PP-g-St-AN / ABS blends are illustrated in **Figure 3.23**. It was observed that PP rich blends show ductile behaviour whereas blends with higher % of ABS (>15%) break before yield point indicating brittle behaviour as observed in PP / ABS blends compatibilized with PP-g-acrylic acid and PP-g-2-HEMA.

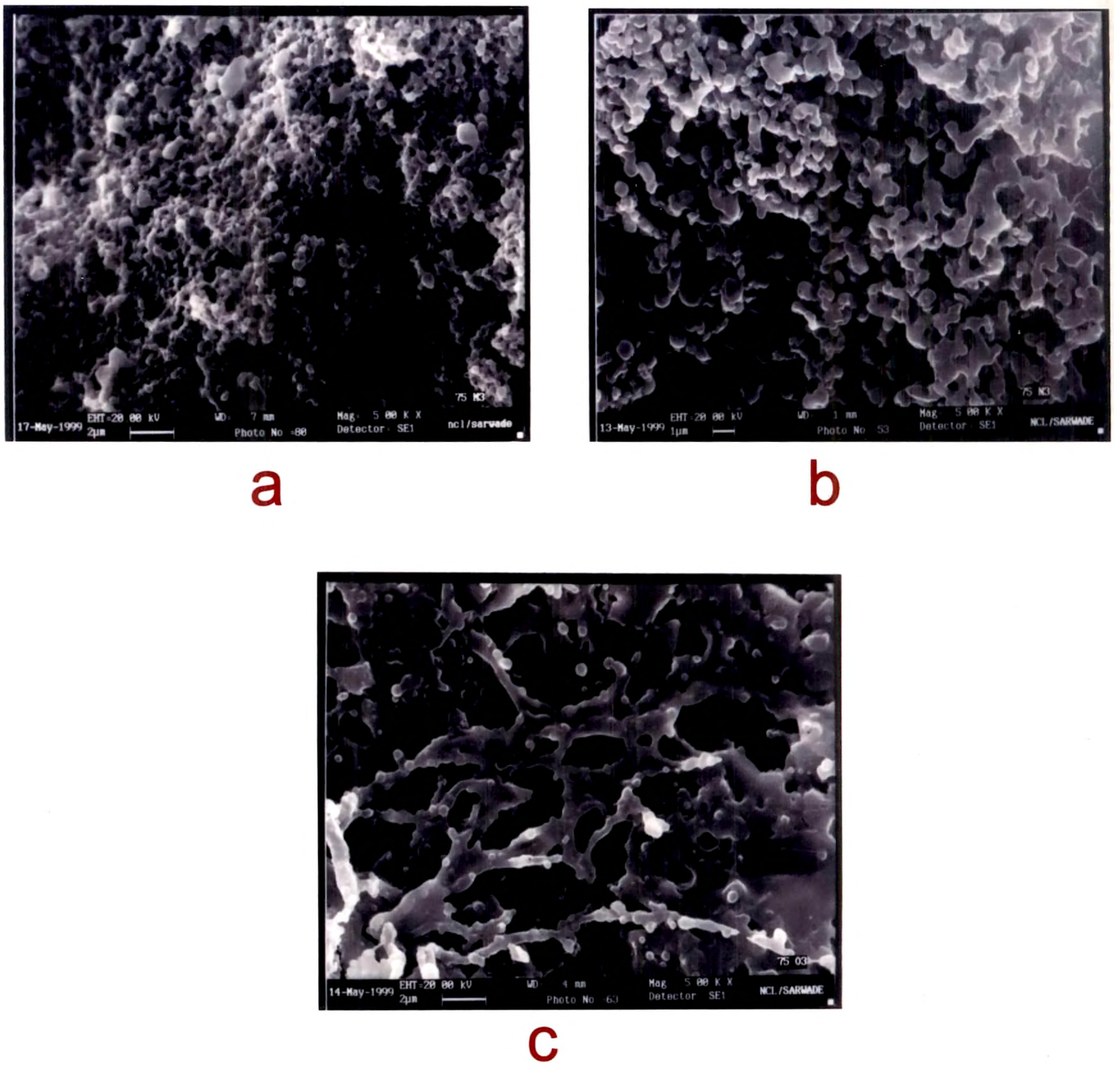


Fig. 3.22 SE micrographs of impact fractured surfaces of PP/ ABS / PP-g-St-AN blends after extraction of ABS in MEK

a : 75 / 25 /2.5; **b :** 75 / 25 /5 ; **c :** 75 / 25 / 7.5

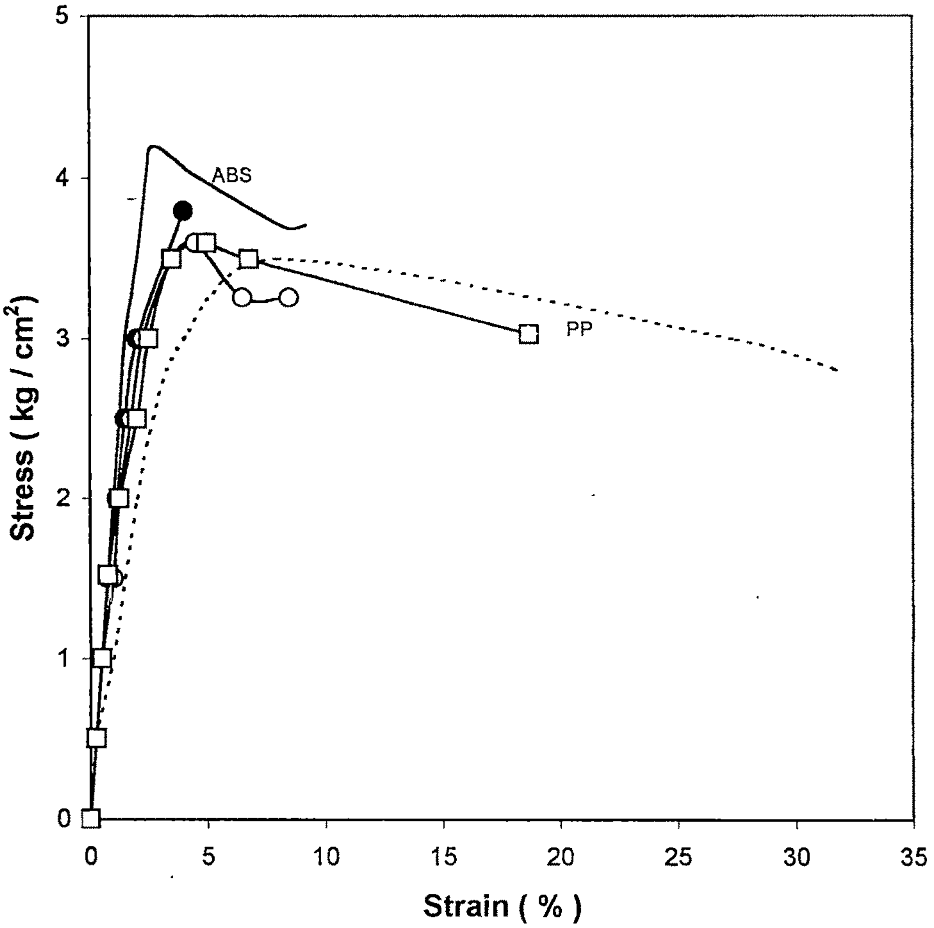


Fig. 3.23 Stress- Strain Curves for PP ABS Blends

— ABS; ----- PP ;

● 75 / 25 / 2 5 PP / ABS / PP-g-St-AN;

○ 90 / 10 / 2.5 PP / ABS / PP-g-St-AN;

□ 90 / 10 / 2.5 PP / ABS / PP-g-St-AN

Due to lower tensile modulus of PP the tensile modulus of all binary and ternary blends was observed to be lower than that of ABS (**Fig.3.24**). However, here also incorporation of PP in ABS does not show considerable effect on modulus but incorporation of ABS in PP shows considerable increase in the modulus of ternary blends compared to PP. The tensile modulus of ternary blends was observed to be higher than that of binary blends at all compositions. Moreover the tensile modulus is higher when the blends were compatibilized with PP-g-St-AN.

Mathematical Modelling

In Neilsen's model[117] a smaller value of $\varnothing_{max}$ represents a larger interface, and large value of $\varnothing_{max}$ represents smaller interface. To see the validity of the proposed models for the system under examination tensile modulus of the blends under study was calculated by using these models and considering the Poisson's ratio υ for PP and ABS as 0.35 and 0.39 respectively. The calculated tensile modulus values were compared with those obtained experimentally (**Figure 3.25**). It was observed that Kerner's model for loosely bound inclusion shows considerable deviation from the experimentally obtained data for binary as well as ternary blends as expected. However, stiffening effect was observed to be more when blends were compatibilised. In addition to the stiffening effect, the factor further responsible for higher tensile modulus in compatibilized blends is increased adhesion at interface and thus homogeneity and finer distribution of dispersed phase.

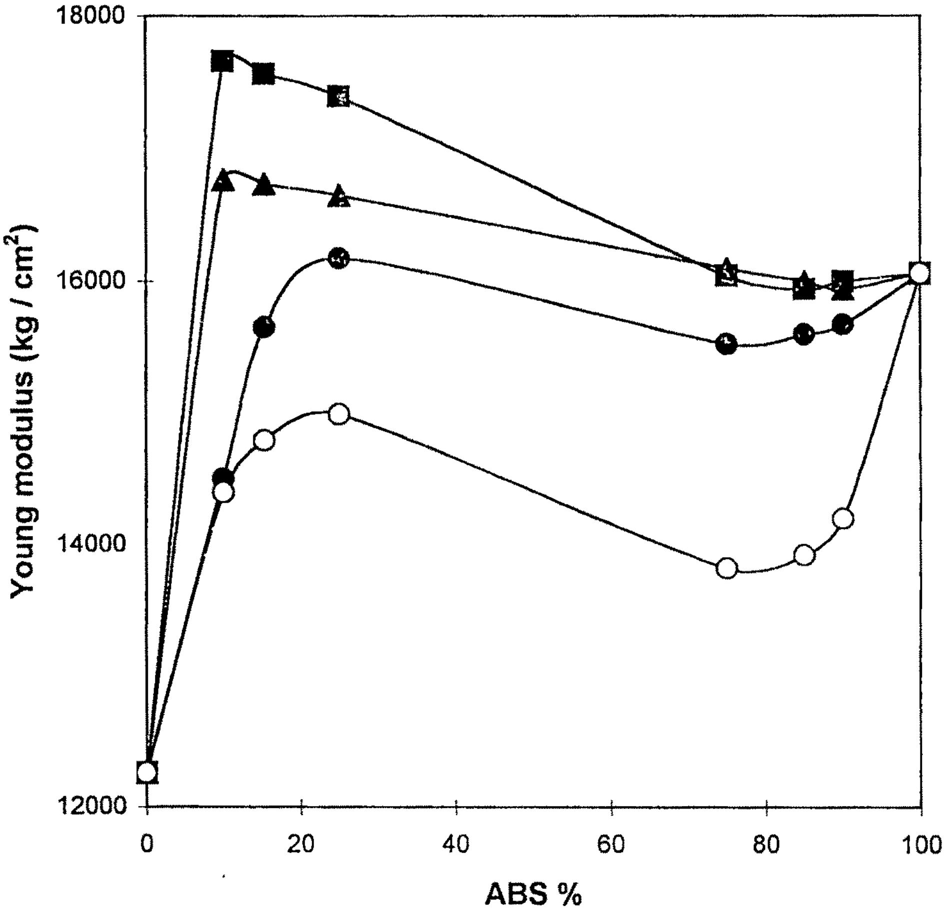


Fig. 3.24 Tensile Modulus of PP/ ABS Blends

PP/ ABS / PP-g-St-AN blends with

(O) 0 %, (●) 2.5 %, (■) 5 % and (▲) 7.5 % PP-g-St-AN

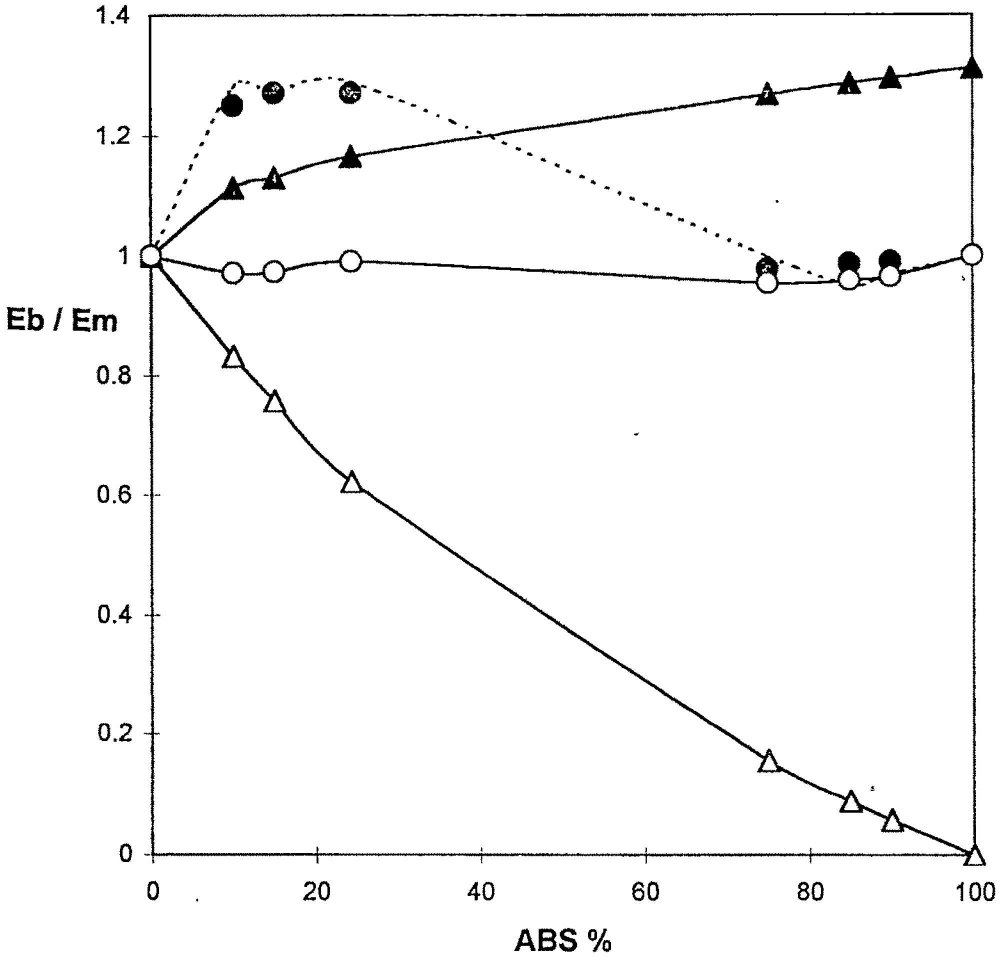


Fig. 3.25 Theoritical Models for the Tensile Modulus of PP / ABS Blends

Kerners model for perfectly bound inclusions (▲)

Kerners model for loosely bound inclusions (Δ)

Neilsen model for rubber dispersed in rigid matrix (----)

PP / ABS blends experimental value (O)

PP / ABS /2.5% PP-g-St-AN blends experimental value (O)

Neilsen's model predicts tensile modulus on the basis of $\varnothing_{max}$ value. The $\varnothing_{max}$ values are adjusted in such a way that the theoretical data match to experimental data. The $\varnothing_{max}$ values used for the calculation of tensile modulus are given in **Table 3.6**. The larger $\varnothing_{max}$ values were obtained for binary blends at all compositions as compared to the compatibilised blends which indicate the coarse particles formation in binary blends (**Fig.3.1.a, b**) whereas finer particles are obtained after compatibilisation (**Fig.3.22.a-c**). It was observed that with increased content of ABS, $\varnothing_{max}$ values go on increasing, indicating decreased volume of the interface, which is immobilised by the discrete phase in the blend. The reciprocal of $\varnothing_{max}$ can be considered as an interaction parameter, which is proportional to $(R+\Delta R)^3$, where R is the radius of the inclusion and ΔR is the depth of interface that is immobilised by the inclusion. For the given value of ΔR, the smaller the size of the inclusion, the smaller the $\varnothing_{max}$ value. (**Table-3.6**). The $\varnothing_{max}$ values were smaller compared to the blends compatibilized through PP-g-acrylic acid and PP-g-2-HEMA indicating finer distribution of dispersed phase, which is supported by **Fig.3.22.**

Impact and Flexural Properties

Flexural modulus and tensile strength were observed to increase with increased concentration of ABS in blends. The toughening effect of ABS increases the flexural modulus of the blends(**Fig.3.26**). The tensile strength was also observed to increase with increasing concentration of ABS in blends. Due to the increase in .adhesion at interface tensile strength of the ternary blends was observed to be higher compared to binary blends (**Fig.3.27**). increse in compatibiliser concentration from 2.5

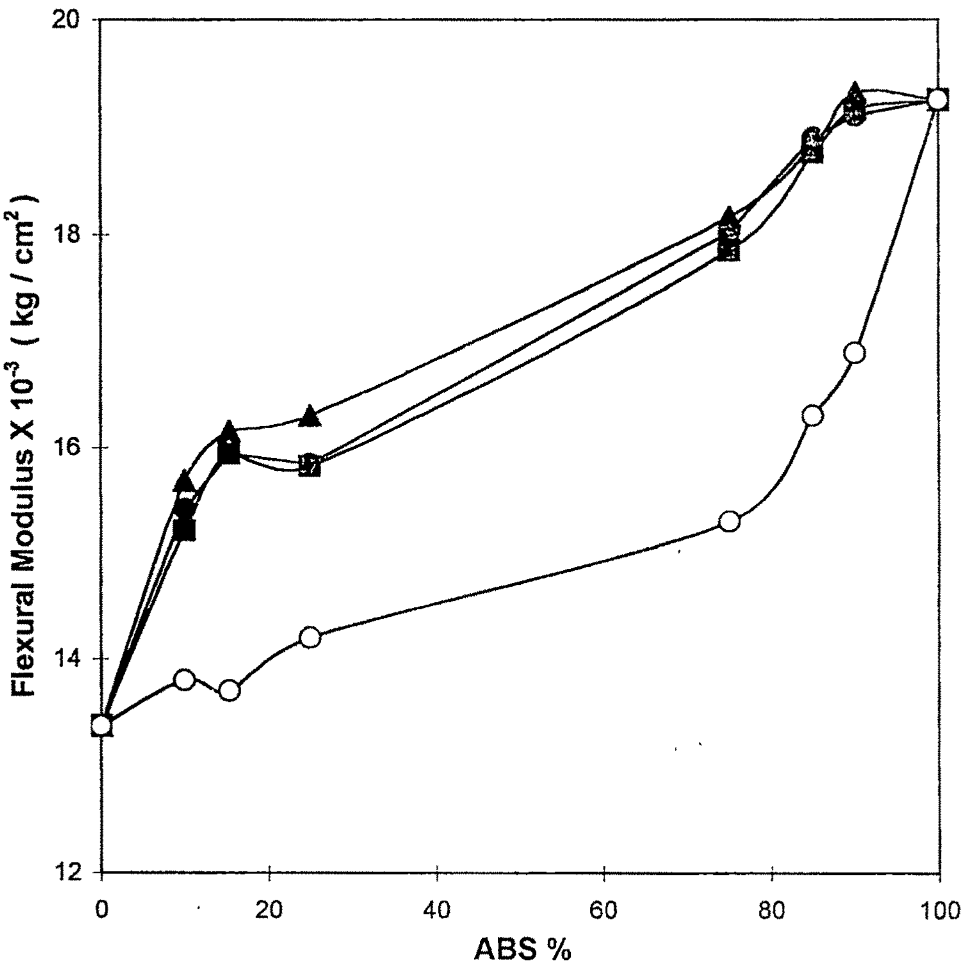


Fig. 3.26 Flexural Strength of PP / ABS Blends

PP/ ABS / PP-g-St-AN blends with

(O) 0 % , (●) 2.5 %, (■) 5 % and (▲) 7.5 % PP-g-St-AN

TABLE 3.6 Adjusted $\varnothing_{max}$ values for PP / PP-g-St-AN / ABS

ABS w % in blends	$\varnothing_{max}$ of PP / PP-g-St- AN / ABS Blends			
	PP-g-St-AN 0 w %	**PP-g-St-AN 2 w %**	**PP-g- St-AN 5 w %**	**PP-g- St-AN 7.5 w %**
10	0.45	0.31	0.37	0.42
15	0.69	0.32	0.389	0.52
25	0.78	0.35	0.40	0.69

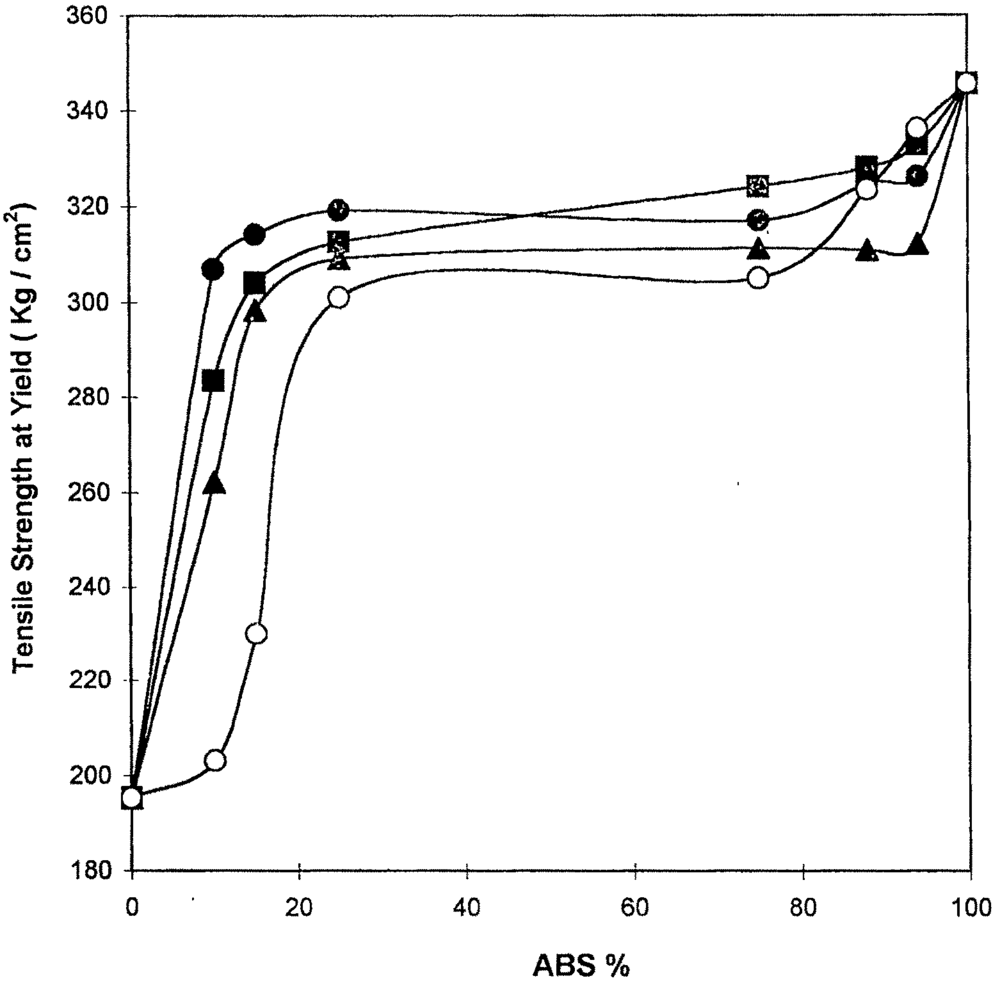


Fig.3.27 Tensile Strength of PP / ABS Blends

PP/ ABS / PP-g-St-AN blends with

(O) 0 % , (◉) 2.5 %, (■) 5 % and (▲) 7.5 % PP-g-St-AN to 5 or 7.5 % did not show improvement in the properties, rather showed decrease in tensile strength.

The tensile strength of PP / ABS / PP-g- St-AN blends was observed to be higher than the PP/ABS blends compatibilised through PP-g-acrylic acid and PP-g- 2-HEMA.

Sharp decrease in % elongation at break was observed in binary as well as ternary blends with incorporation of ABS into PP. However, decrease in % elongation was more critical in binary blends. (**Fig.3.28**). Upon addition of the compatibilizer the decrease in % elongation was observed to be less due to the plastication of blends.

Fig.3.29 illustrates the impact strength of PP/ABS binary and PP / PP-g-St-AN / ABS ternary blends as a function of ABS content in blends. As seen from **Fig.3.29**, 2.5% compatibilizer is sufficient for toughening the blends. Whereas, further incorporation of compatibilizer in blend does not show improvement in impact strength but rather decreases the impact strength. This can be explained from the observed smaller particle size of the dispersed phase at 2.5% compatibilizer concentration (**Fig.3.22**). The decrease in impact strength of blends with increased % compatibilizer can be attributed to the formation of aggregates of compatibilizer in the bulk phase after a critical concentration of compatibilizer **Fig.3.22** shows the effect of compatibilizer concentration on particle size. At 2.5 w % compatibilizer the particle size is small and is increased with addition of 5 w % of compatibilizer and particles were deformed on further addition of compatibilizer. Thus this structure shows the poor distribution of particles

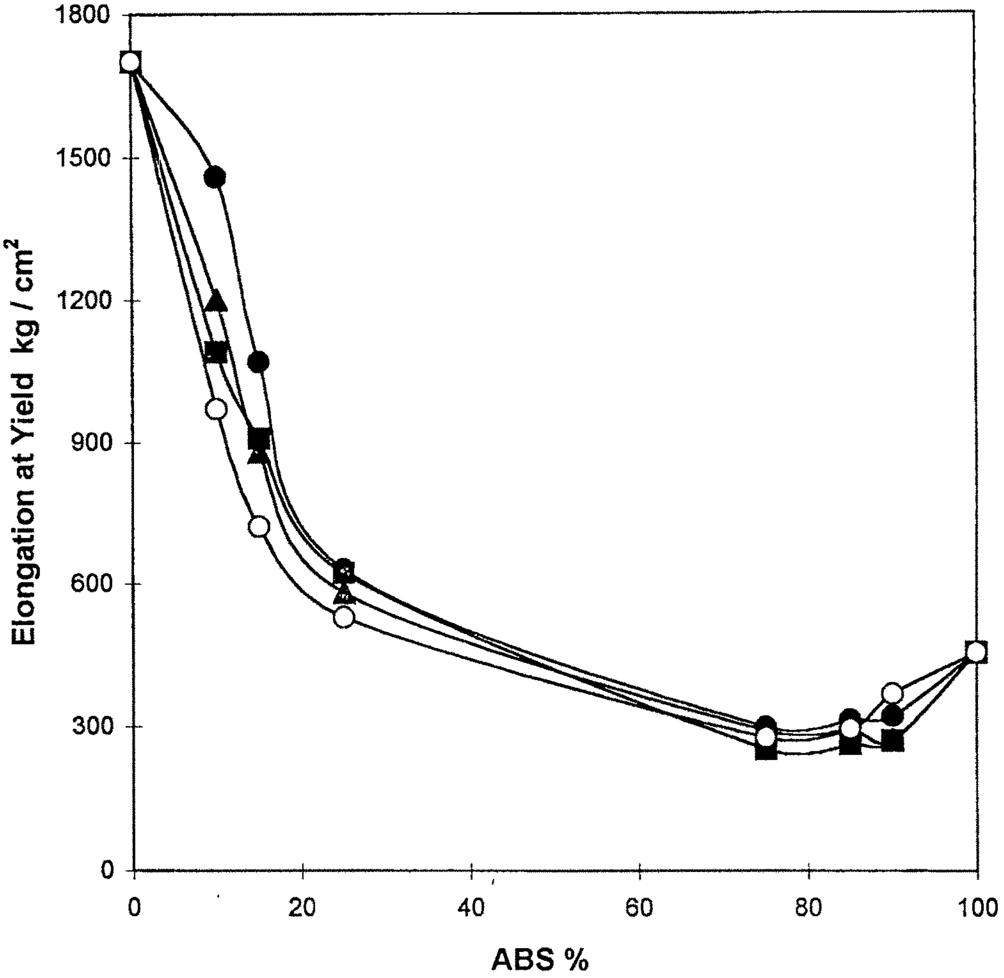


Fig. 3.28 Elongation at Yield of PP / ABS Blends

PP/ ABS / PP-g-St-AN blends with

(O) 0 % , (●) 2.5 %, (■) 5 % and (▲) 7.5 % PP-g-St-AN

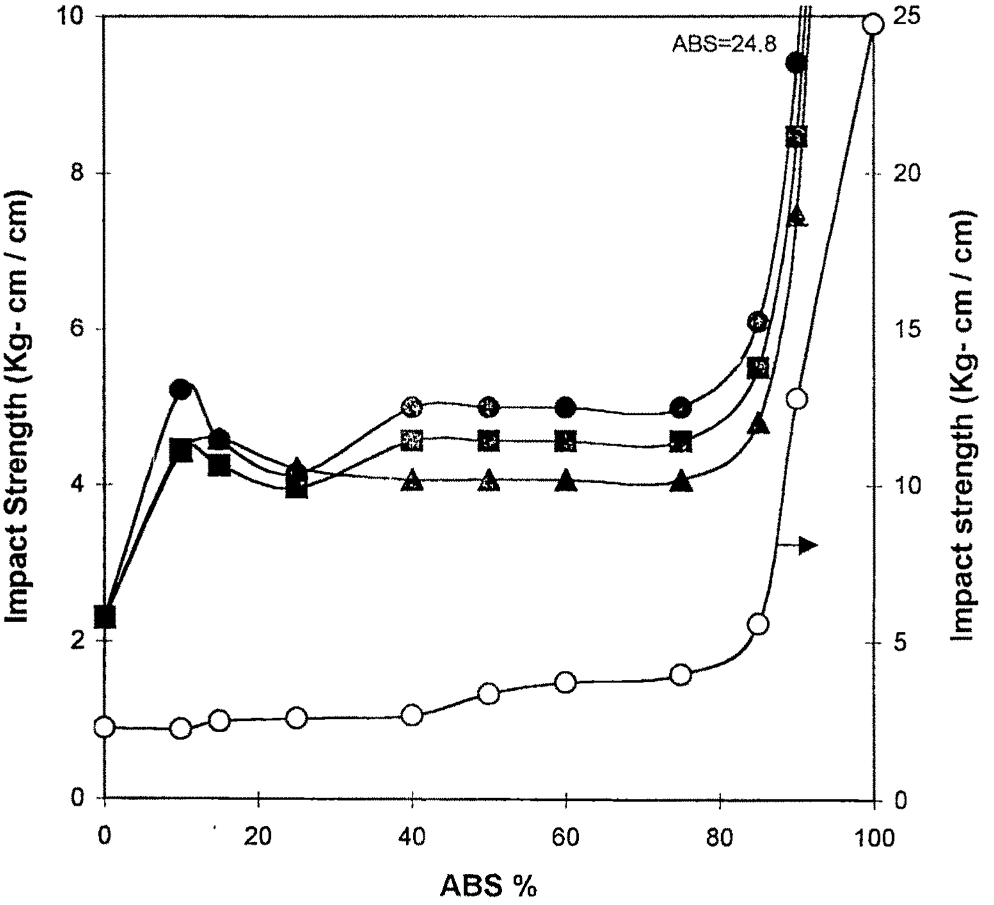


Fig. 3.29 Impact Strength of PP / ABS Blends

PP/ ABS / PP-g-St-AN blends with

(O) 0 % , (●) 2.5 %, (■) 5 % and (▲) 7.5 % PP-g-St-AN

and poor adhesion at interface which does not contribute for dissipation of impact energy. The similar observation was made by Asaletha et.al.[113] and Thomas et.al.[114] for PP/NR blends in which the size of dispersed particle decreases only up to certain concentration of compatibilizer.

- PP-g-St-AN is also a effective compatibiliser for PP/ ABS blends
- Spherical and finer dispersion of ABS phase in PP rich blends was observed
- Higher modulus was observed as compared to earlier cases
- But not much improvement in impact strength was observed in the case of PP-g- St-AN as a compatibiliser

3.8 Conclusion

PP/ ABS blends are incompatible at all ratios due to the differences in the nature of their constituents with respect to polarity, solubility and interfacial tension. The blends show considerable variations in mechanical properties, particularly in PP rich region upon addition of 2.5% to 7.5% PP-g-acrylic acid as a compatibiliser. The blends exhibit good tensile behaviour at 10-15% ABS content due to good enough adhesion at interface between two phases. The experimental data for tensile modulus of compatibilised blends agree with the calculated values from Kerners' model for these blends show the adhesion at interface between PP and ABS. The $\emptyset_{max}$ values obtained through Nielsens' model indicates large and coarse particles formation in binary blends whereas smaller particles formation is observed after compatibilisation. The particle size of the dispersed ABS phase decreases upto 5 % of the compatibiliser concentration and there after increases which can be attributed to the formation of aggregates of compatibiliser in the bulk phase after a critical concentration of compatibiliser. The blends show the ductility upto 10-15 % of ABS in blends and after that they become brittle in nature even after compatibilisation. The ABS rich blends show poor mechanical properties and also poor morphology and can not be of commercial use.

Use of PP-g-2-HEMA as a compatibiliser for PP / ABS blends showed improvement in izod impact strength, tensile strength and tensile modulus. The 2.5% concentration of compatibiliser was observed to be critical for the improvement in the properties. Kerner's model for perfect adhesion was observed to be applicable only for PP rich blends, whereas The $\varnothing_{max}$ values obtained through Neilsens' model for perfect adhesion indicate large and coarse particles formed in binary blends whereas smaller particles formed after compatibilisation which was supported by SE photographs.

PP-g-St-AN also showed improvement in izod impact strength, tensile strength and tensile modulus properties of PP / ABS blends. The 2.5% concentration of compatibiliser was observed to be critical for the improvement in the properties. Though the impact strength was observed to be less as compared to the blends compatibilised with PP-g-2-HEMA but Young's modulus was observed to be very high even higher than ABS. Like in PP / ABS / PP-g-2-HEMA blends, $\varnothing_{max}$ values obtained through Neilsens' model for perfect adhesion indicates large and coarse particles formed in binary blends whereas smaller particles formed after compatibilisation which was supported by SE photographs. Compatibilisation of blends resulted into smaller size of dispersed phase (ABS) in PP rich blends. The particles were observed to be finer and homogeneous, and extraction of ABS dispersed phase by MEK from PP rich blends was not possible.

Over all PP / ABS ternary blends show better performance in the order PP/ ABS / PP-g-2-HEMA > PP / ABS / PP-g-St-AN > PP / ABS / PP-g-acrylic acid, which is shown in table.

Mechanical properties of PP/ABS binary and ternary blends

Properties	PP/ABS 90/10	PP/ ABS / PP-g-2-HEMA 90/10/2.5	PP/ ABS / PP-g-St-AN 90/10/2.5	PP/ ABS / PP-g-acrylic acid 90/10/2.5
Particles size	7.5	5.6	4.2	-
Impact strength	2.2	3.4	7.5	4.4
Youngs' modulus	12440	14380	15673	16496
Tensile strength	203.1	308.0	286.0	262.2
Elongation at Yield	1605	807	1347	1400
Model useful	Nielsens'	Kerners' & Nielsens'	Kerners' & Nielsens'	Kerners' & Nielsens'

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