Polym. Bull. (2012) 68:859–877
DOI 10.1007/s00289-011-0656-z

ORIGINAL PAPER

Studies on impact modification and fractography of solution cast blends of PVC and NR/PU block copolymers

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Received: 20 April 2011 / Revised: 29 August 2011 / Accepted: 11 October 2011 /

Abstract Segmented polyurethanes based on toluene diisocyanate (TDI) with three different chain extender diols, viz., propylene glycol (PG), 1,4-butanediol (1,4-BDO), and 1,3-butanediol (1,3-BDO) were synthesized by a two-step, solution polymerization method. These different NR-*b*-PU block copolymers were incorporated into PVC at various compositions by the solution blending method. These blend systems were subjected to FTIR analysis, DSC, tensile testing, tensile impact measurements, and tensile impact fracture studies by SEM. It was observed that systems showed modification in tensile impact properties. Optimum impact properties were shown at concentrations 6–8% of the block copolymer. At higher compositions there is deterioration in impact properties. High impact properties showed by these blends are attributed to the optimum level of compatibility achieved between the blend components. Tensile impact fracture studies revealed that failure pattern for these blend system transitioned from brittle to ductile fracture. Blends up to 10 wt% of block copolymer showed partially compatible heterogeneous nature exhibiting domain morphology. Blends with higher block copolymer content showed deterioration in tensile strength, modulus, yield strength, and tensile impact strength due to higher particle size of the agglomerated rubber soft segments of the block copolymer.

Keywords PVC · Polyurethanes · Block copolymers · Blends · Mechanical properties · FT-IR · Fractography · Impact strength

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Introduction

The use of rigid polyvinyl chloride (PVC) is enabled by its modification through polymeric additives. These additives form partially miscible blends with PVC which display phase separation but with a significant degree of polymer mixing on a molecular level producing chemically compatible phase with useful properties. Polymeric additives are mainly used as processing aids and impact modifiers. Where as processing aids show compatibility with PVC without plasticizing action, impact modifiers show only limited compatibility by virtue of which the blend forms multiphase systems. The polymeric additives are capable of exerting intermolecular forces such as donor–acceptor interaction, dipole–dipole interaction, and hydrogen bonding with PVC.

There are many reports in the literature concerning PVC/polyurethane (PU) blends [1–4]. Zhu et al. [1] studied three different PUs and the compatibility of blends of these PUs with PVC was studied. Miscibility of segmented PUs (SPUs) and PVC or functionalized PVCs (FPVCs) were studied with dynamic mechanical analysis, differential scanning calorimetry (DSC), and X-ray diffraction [2]. The miscibility of the blends depended greatly on the hard-segment content of SPU and the existence of the functional groups. In another work semi-interpenetrating polymer networks (semi-IPNs) of polyurethane anionomers (IPU) with PVC were synthesized and characterized by Fourier-transform infrared spectrophotometer (FTIR), thermo gravimetric analysis (TGA), and mechanical studies [3]. Tensile strength and hardness increase with increasing NCO/OH ratio and ionic content of the PUs. Petrovic et al. [4] blended a polyester urethane elastomer with rigid PVC and the miscibility of the components studied over the entire range of compositions. The feasibility of plasticization of rigid PVC with a reclaimed PVC–PU was studied by Grigoreva et al. [5]. Ternary blends of thermoplastic PU (TPU) and a PVC/nitrile rubber blend were investigated in another work [6]. The fracture toughness was investigated, the components and the miscible blends showed good fracture toughness, whereas the other blends showed lower toughness. Similar behavior was observed for the tensile properties. The possibility of PVC plasticization and modification by regenerated PVC/polyurethane rubber (PVC/PUR) blends, obtained after partial thermo chemical destruction of the PU foam-backed PVC-sheet, has been studied by Grigoryeva et al. [7]. It has been established that PVC/PUR blends can be reused as an effective polymer plasticizer for PVC resin and as a modifier for plasticized-PVC (p-PVC). In another study, a novel reactive blending process was developed for producing PVC/TPU blends [8]. Because of reaction-induced phase separation, the resulting partially miscible PVC/TPU blends were characterized by heterogeneous, multiphase morphologies and they exhibited excellent tensile properties intermediate between that of neat PVC and TPU. Pielichowski and Janowski [9] studied a series of semi-IPNs of PU and PVC. The compatibility of blends of p-PVC and TPU was investigated using a dynamic mechanical analyzer and scanning electron microscopy by Kim et al. [10]. It was concluded that the compatibility of p-PVC and TPU is dependent on the ratio of hard to soft segments in TPU. Fracture toughness and properties of blends of p-PVC and TPU were investigated in a reported work [11]. Blending of TPU with p-PVC improved tensile strength, impact strength, abrasion resistance, and thermal stability, with small decline of tensile modulus and hardness. Solution-cast specimens of PVC/PU blends were studied by means of infrared, DSC, and dynamic mechanical measurements [12].

The low impact strength of PVC has caused long standing problems in the processing and application of unplasticized PVC**.** This has been overcome with the help of impact modifiers evolved out over a period of time during the development of processing techniques. The impact modifiers are generally polymeric materials which are only partially compatible with PVC. It has been widely reported that the morphology of polymer blends has a strong influence on the impact properties [13–15].

We have synthesized a new class of NR/PU block copolymers with low PU hard segment content. It is expected that these block copolymers with 30% PU hard segment which is found to be miscible with PVC and 70% rubbery soft segment which is immiscible would be suitable candidates in modifying the impact properties of PVC. So this study involves the characterization of blend systems in terms of the impact properties and to study the effect of variation in the block copolymer content and the nature of block copolymer on these characteristics. It also aims to find out the optimum composition of these three different block copolymers so as to achieve maximum impact modification of PVC.

Experimental

Materials

PVC with K value 65, $\overline{M}_W = 1.4 \times 10^5$, and density 1.37 (M/s Chemicals and Plastics, Chennai, India) was used for blending. Natural crumb rubber (ISNR-5) with $\overline{M}_W = 8.2 \times 10^5$, intrinsic viscosity in benzene at 30 °C = 4.45 dL/g, was received from Rubber Research Institute of India (RRII), Kottayam, India. Liquid natural rubber with $\overline{M}_W = 4600$ is obtained by depolymerization of NR [16]. Tetrahydrofuran (THF) soluble block copolymers from toluene diisocyanate (TDI), with chain extender diols, viz., propylene glycol (PG), 1,4-butanediol (1,4-BDO), and 1,3-butanediol (1,3-BDO), were synthesized by solution polymerization [17]. TDI was an 80/20 mixture of 2, 4- and 2, 6-isomers. This was supplied by Merck (Germany) and used as received. PG obtained from E. Merck, India and 1,4-BDO supplied by Fluka (Switzerland). 1,3-BDO was supplied by Riedel-dettaën (Germany). These diols dried with anhydrous CaO and then distilled under reduced pressure before use. Dibutyltin dilaurate (DBTDL) was supplied by Fluka (Switzerland) and used as catalyst without further purification. Chloroform was laboratory grade, which was supplied by Merck. India Ltd., Bombay (India). It was dried with anhydrous calcium oxide and then distilled before use. Methanol (Reagent grade) was obtained from Merck India Ltd. It was used without further purification. Hydrogen peroxide (30%) was obtained from Merck India Ltd. Toluene and THF (Reagent grade) supplied by Merck India Ltd. was distilled before use.

Methods

Synthesis of block copolymers

Soluble block copolymers from TDI, with chain extender diols, viz., PG, 1,4-BDO, and 1,3-BDO, were synthesized by solution polymerization. Maintaining low hard segment content and keeping optimum NCO/OH ratio, formation of linear, flexible elastomers is achieved [17]. The block copolymers were synthesized with approximately constant composition, viz., 70/30 of the soft and hard segments. The composition of the block copolymer samples prepared in this study and their characteristics is presented in Table 1.

Preparation of blends

Three series of blends of PVC and NR-*b*-PU block copolymers were prepared from the common solvent THF as follows. A 3% (w/v) solution of PVC in THF was prepared. This solution was then added to the block copolymer solution in THF at various compositions. It was thoroughly mixed using a magnetic stirrer for 12 h at 50 °C and cast on glass plates. The samples were then dried in vacuum at 70 °C for 2 days to remove the traces of residual solvent. Composition of the blends prepared is shown in Table 2.

Measurements

FTIR analysis

IR spectra were recorded at room temperature on a Shimadzu FTIR-8400S, spectrometer (Japan) by averaging 50 scans at a resolution of 2 cm^{-1}.

Differential scanning calorimetry (DSC)

The DSC measurements were done using a Mettler Inc. (TA 300) micro-calorimeter (Germany) at a programmed heating rate of 10 °C/min. The measurements were carried out in the temperature range, -100 to 100 °C under dry nitrogen atmosphere (25 mL/min) using alumina crucibles. The sample weight was 4–5 mg and the first heating scans are reported in this study.

Table 1 Composition and characteristics of NR-*b*-PU block copolymers

Sample	NCO/OH ratio	Hard segment (wt%)	Soft segment (wt%)	[η] (dL/g)	$\overline{M}_n$	$\overline{M}_w$	Dispersity
NR-*b*-PU_1	1.08	31.14	68.86	0.2603	14000	31400	2.242
NR-*b*-PU_2	1.08	31.88	68.12	0.2752	14877	33640	2.261
NR-*b*-PU_3	1.08	31.88	68.12	0.2656	14113	31810	2.253

Table 2 Composition of PVC/NR-*b*-PU blends

Sample designation	Components and composition	
	PVC	NR-*b*-PU_1/NR-*b*-PU_2/NR-*b*-PU_3
PVC/NR-*b*-PU_1 (98/2)	98	2
PVC/NR-*b*-PU_1 (96/4)	96	4
PVC/NR-*b*-PU_1 (94/6)	94	6
PVC/NR-*b*-PU_1 (92/8)	92	8
PVC/NR-*b*-PU_1 (90/10)	90	10
PVC/NR-*b*-PU_1 (80/20)	80	20
PVC/NR-*b*-PU_1 (70/30)	70	30
PVC/NR-*b*-PU_1 (60/40)	60	40
PVC/NR-*b*-PU_1 (50/50)	50	50
PVC/NR-*b*-PU_2 (98/2)	98	2
PVC/NR-*b*-PU_2 (96/4)	96	4
PVC/NR-*b*-PU_2 (94/6)	94	6
PVC/NR-*b*-PU_2 (92/8)	92	8
PVC/NR-*b*-PU_2 (90/10)	90	10
PVC/NR-*b*-PU_2 (80/20)	80	20
PVC/NR-*b*-PU_2 (70/30)	70	30
PVC/NR-*b*-PU_2 (60/40)	60	40
PVC/NR-*b*-PU_2 (50/50)	50	50
PVC/NR-*b*-PU_3 (98/2)	98	2
PVC/NR-*b*-PU_3 (96/4)	96	4
PVC/NR-*b*-PU_3 (94/6)	94	6
PVC/NR-*b*-PU_3 (92/8)	92	8
PVC/NR-*b*-PU_3 (90/10)	90	10
PVC/NR-*b*-PU_3 (80/20)	80	20
PVC/NR-*b*-PU_3 (70/30)	70	30
PVC/NR-*b*-PU_3 (60/40)	60	40
PVC/NR-*b*-PU_3 (50/50)	50	50

Stress–strain behavior

Stress-strain behavior was studied on a Zwick 1474 Universal Testing Machine (Germany) as per ASTM D 412-80 test method at a constant cross head speed of 500 mm/min. Five dumb-bell shaped specimen of every sample were used to determine the Young’s modulus, tensile strength, and elongation at break and the average value was taken as the result.

Tensile impact measurements

Tensile impact testing of the samples was done according to DIN 53448 test method using a CEAST 6545/000 model tensile impact tester. The energy utilized to break the test specimen in this method was delivered by a single swing of a calibrated pendulum of the standard tension impact machine. The pendulum used could deliver a maximum of 15 J and the speed of the test was 3.7 ms^{-1}.

SEM analysis

The fracture surface of the tensile impact specimen was sputter coated with gold immediately after testing and SEM observation was made using a JOEL JSM -35C scanning electron microscope and the fractographs were taken along the direction of the fracture propagation adjusting the tilt angle to 33° in all cases.

Results and discussion

Blends of PVC and NR-*b*-PU block copolymers were prepared in two categories. First category blends with weight percent ranging from 10 to 50 of NR-*b*-PU. In this category, there are five series of blends each composition varying by 10%. Impact values of this series are used to describe the general trend. The effect of blend composition and the nature of the block copolymer on the tensile impact strength of PVC are discussed in this section. Based on these observations, another category blend series (Series II) have been prepared with block copolymer contents with 2–10 wt%. Impact behavior of this second series is studied and the values are used to ascertain the exact composition giving maximum impact properties for the three series.

All the blends were subjected to tensile impact measurements and SEM studies. The effect of blend composition and nature of the PU hard segment of the block copolymer on the tensile impact strength of PVC are discussed.

FTIR

FTIR spectroscopic investigations are carried out on the individual components and all the three series of PVC/NR-*b*-PU blend systems. Figure 1a–e shows the FTIR spectra of the individual components, and selected blend compositions of a representative blend series, viz., PVC/NR-*b*-PU_2 blends. The FTIR spectrum of PVC (Fig. 1a) showed characteristic peaks at 2700–3000 cm^{-1} which corresponds to aliphatic C–H stretching (C–H, C–H_2). The stretching frequency at 1434 cm^{-1} corresponds to C–H stretching of the syndiotactic region of PVC. The peak at 1260 cm^{-1} is assigned to C–C stretching. The characteristic peak at 950 cm^{-1} corresponds to methylene rocking vibration. The bands more characteristic of the spectrum of PVC are those in the region of 600–700 cm^{-1}, corresponding to C–Cl stretching vibrations.

In the IR spectrum of the block copolymers (Fig. 1b), the band between 3400 and 3300 cm^{-1} is due to the NH bond in the PU. A very weak shoulder occurs around 3360 cm^{-1} indicating the presence of a few number of free NH groups. All the three samples show broad N–H stretching bands. NH absorption bands for all the synthesized block copolymers are found at 3378–3354 cm^{-1}. The IR spectra show typical bands in the carbonyl (C=O) vibration region (1725–1722 cm^{-1}), which are attributed to the urethane group, and a band around 1600 cm^{-1}, which is assigned to

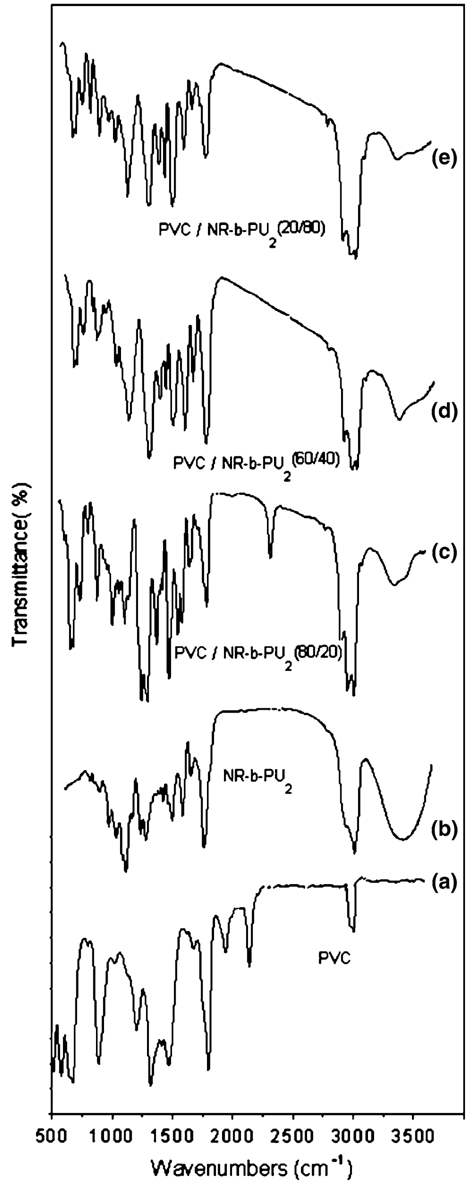

Fig. 1 FTIR spectra of PVC/NR-*b*-PU$_2$ blends and blend components. (*a*) PVC, (*b*) NR-*b*-PU$_2$, (*c*) PVC/NR-*b*-PU$_2$ (80/20), (*d*) PVC/NR-*b*-PU$_2$ (60/40), and (*e*) PVC/NR-*b*-PU$_2$ (20/80) blends

the C=C bond. Band in the range 1048–1061 is attributed to C–O–C stretching vibrations in the PU hard segments.

FTIR analysis of PVC/NR-b-PU blends

As all the three series of blends studied gave similar results, results for PVC/NR-*b*-PU$_2$ blend series are described here. Blends showed all the characteristic peaks of the component polymers as shown in Fig. 1c–e. The shape and position of most of the bands in both spectra are very similar although some differences exist in the relative intensity and shape of the bands. For the PVC/NR-*b*-PU_2 blends the major peaks appear at, for example, ~3260 (ν N–H), 2962 (ν CH_2), ~1700 (ν C=O), ~1430 (ν α –C–H), ~628 (ν C–Cl, isotactic 659 (ν C–Cl, syndiotactic) and ~1060 (ν C–O–C) cm^{-1}.

Certain FTIR spectral peaks in the blends are found to undergo frequency shift when compared to the individual component polymers, viz., PVC and the respective block copolymer. Noticeable shift occurs for, C–Cl stretching at 638 and 679 cm^{-1} of PVC and N–H stretching band of the PU segments of the block copolymer. In the blends, the 638 band of virgin PVC shifts to a lower frequency in the blends. For example, for the 20/80 blend the band occurs at 630 cm^{-1}, frequency shift $\Delta\nu$ being 10 cm^{-1}. Similar frequency shift occurs to C–Cl (syndiotactic) stretching band also, the shift, $\Delta\nu$, is 21 cm^{-1} for the 20/80 composition. Similarly, N–H stretching band of the PU segments also shows frequency shifts and band broadening compared to the component polymers. The broad band between 3567 and 3126 cm^{-1} centered around 3310 cm^{-1} is due to the N–H bond of the PU hard segment of the NR-*b*-PU_2 block copolymer. In the blends these bands show frequency decrease. The frequency shift is found to be independent of compositional changes while intensity of the absorptions varies according to compositional changes. NH bands of the blends suffer band broadening when compared to the pure block copolymer. For example, for the 80/20 blend N–H stretching band occurs in the region 3374–3239 cm^{-1} centered around 3262 cm^{-1} and for the 20/80 blend the absorption is at 3379–3229 cm^{-1} centered around 3260 cm^{-1}. This shows that some of the inter-PU H bonds in the PU hard segments of the block copolymer are broken and are used for secondary polar interactions with C–Cl bonds of PVC. The relative intensities of the bonded N–H band also decrease accompanied by band broadening. It should be noted that the weak shoulders indicative of some free N–H bonds present in the pure block copolymer spectrum is absent in the case of blends. Band broadening accompanied by lowering in absorption frequency of C–Cl of PVC and NH bands of PU suggest that by blending hydrogen bonding occurs between the constituents. This polymer–polymer interaction leads to miscibility of PVC and PU segments.

DSC

These observations are further supported by DSC analysis. The DSC analysis data of selected samples are given in Table 3. PVC exhibits a T_g value of 81.9 °C. DSC results show that the blends exhibited two main transitions. Transition around 75–60 °C corresponds to glass-transition temperature (T_g) for the PVC phase. The T_g values decreased from 74.5 to 60.5 °C as the weight percent of block copolymer was increased from 20 to 80. Blends exhibit single intermediate T_g values. The second transition, the sub-ambient transition occurring at around −51 °C in the DSC thermograms of the PVC/NR-*b*-PU_3 blends is that of the NR soft segments of the block copolymer. The DSC results of the other two series blends samples, viz., PVC/NR-*b*-PU_2 and PVC/NR-*b*-PU_1, show the same pattern as PVC/NR-*b*-PU_3 samples. DSC results show that there is a single glass-transition temperature (T_g) in

Table 3 T_g values of PVC/NR-*b*-PU blends

Blends and compositions	T_g (°C)	
	NR phase	PVC phase
PVC/NR-*b*-PU_1 (80/20)	−55	74.4
PVC/NR-*b*-PU_1 (20/80)	−52	60.5
PVC/NR-*b*-PU_2 (80/20)	−56	76.4
PVC/NR-*b*-PU_2 (20/80)	−53	64.5
PVC/NR-*b*-PU_3 (80/20)	−54	70.1
PVC/NR-*b*-PU_3 (20/80)	−52	60.1

the region of 76–60 °C, for the PVC and PU phases evidencing the miscibility of these two phases.

Stress–strain behavior

Figure 2 shows the stress–strain curve of PVC/NR-*b*-PU_3 blends. It is to be noted that the tensile properties of PVC stand modified in these blend systems. However, it is observed that in the region of improvement in impact strength there is no major sacrifice in tensile strength and modulus of elasticity. For example, tensile strength values of NR-*b*-PU_1 blends are 38.6, 37.6, 38.4, 37.2, and 35.6 N/mm^2 for the 98/2, 96/4, 94/6, 92/8, and 90/10 compositions and for the NR-*b*-PU_3 series these values are 38.9, 38.4, 38.6, 37.6, and 35.7 N/mm^2, respectively, compared to 39 N/mm^2 of virgin PVC. Modulus of elasticity values is almost same. This is because, at these compositions, the tensile properties are mainly controlled by PVC phase though the rubber phase exerts controlling effect on the impact properties. Figure 2 also shows

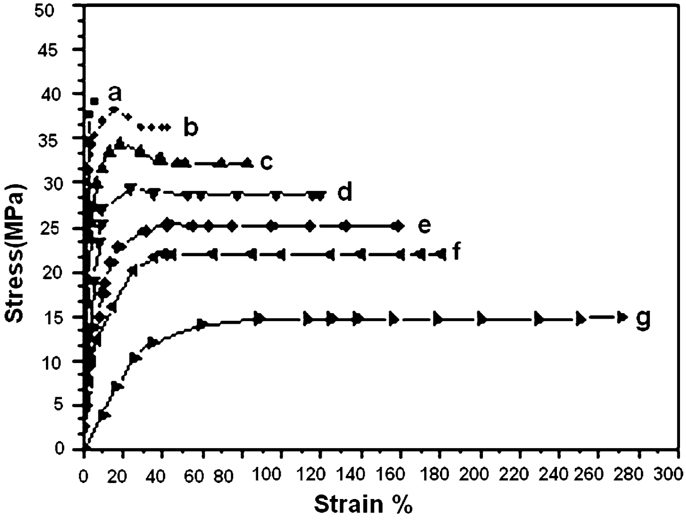

Fig. 2 Stress–strain curves of PVC/NR-*b*-PU_3 blends

that the yield behavior of PVC becomes modified with the addition of the block copolymer. Brittle fracture of virgin PVC is turned into ductile fracture in the presence of rubber as indicated by the yielding behavior shown by the blends. Yielding leads to viscous energy dissipation process enabling the blend systems to absorb large quantity of impact energy. However, excessive increase in block copolymers lowers impact strength because it affects the integrity of the PVC matrix which undergoes rapid failure.

Tensile impact analysis

Tensile impact strength versus blend composition for all the three NR-*b*-PU blend series is shown in Fig. 3a–c. There is an increase in impact strength when compared to virgin PVC up to 10% rubber content. After this there is a progressive decrease. For example, PVC NR-*b*-PU_1 (90/10) and PVC/NR-*b*-PU_1 (80/20) show impact strengths 412 and 345 J/m, respectively, when compared to 320 J/m of virgin PVC. The other compositions show lower values, values being 315, 275, and 255 J/m.

Variation of tensile impact strength versus blend composition for PVC/NR-*b*-PU_2 blend series is shown in Fig. 3b. PVC/NR-*b*-PU_2 blends also exhibit the same trend as PVC/NR-*b*-PU_1 blends. But the tensile impact values for all the compositions are slightly lower when compared to the latter. For example, the tensile impact values for (90/10), (80/20), (70/30), (60/40), and (50/50) compositions are 402, 335, 310, 265, and 245 J/m, respectively, compared to 412, 345, 315, 275, and 255 J/m for PVC/NR-*b*-PU_1 blends.

Figure 3c represents the variation of tensile impact strength with blend composition for PVC/NR-*b*-PU_3 blends. Tensile impact behavior of these blend systems also shows identical pattern as that of PVC/NR-*b*-PU_1 and as PVC/NR-*b*-PU_2 blends, except in the fact that they shows highest tensile impact values for all

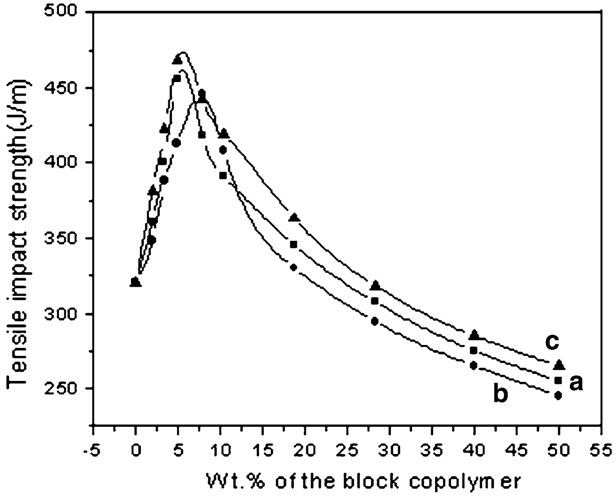

Fig. 3 Variation of tensile impact strength with % composition of block copolymer for (*a*) PVC/NR-*b*-PU_1, (*b*) PVC/NR-*b*-PU_2, and (*c*) PVC/NR-*b*-PU_3 blends

the compositions when compared to the other two block copolymer blends. For example, for the series I blends, the tensile impact values for (90/10), (80/20), (70/30), (60/40), and (50/50) compositions are 402, 335, 310, 265, and 245 J/m, respectively, compared to 420, 363, 318, 285, and 265 J/m for PVC/NR-*b*-PU_3 blends. In both the cases impact strength increases with the block copolymer content to reach a maximum and then decreases slightly with the addition of more block copolymer. Same trend is observed for blends containing 30% block copolymer. In all these three series the maximum impact modification occurs for the (90/10) composition. The values are 412, 402, and 421 J/m, respectively, for PVC/NR-*b*-PU_1, PVC/NR-*b*-PU_2, and PVC/NR-*b*-PU_3 series. When the block copolymer content of the blend is 40 and 50%, impact strength decreases continuously as shown in the figure.

In PVC/NR-*b*-PU_1 (98/2), PVC/NR-*b*-PU_1 (96/4), PVC/NR-*b*-PU_1 (94/6), and PVC/NR-*b*-PU_1 (92/8) blends, the impact strength increases with the block copolymer content. A maximum is found at (94/6) composition. Thus, in this series of blends PVC/NR-*b*-PU_1 (94/6) composition seems to be the best candidate for imparting the highest impact strength to PVC. For PVC/NR-*b*-PU_2, the impact strength maximum is found at (92/8) composition and PVC/NR-*b*-PU_3 blends exhibited a maximum value at 6 wt% of block copolymer. These variations may be explained on basis of the PU hard segment nature caused by the variation in the diol structure. More efficient packing of the hard domains in NR-*b*-PU_2 block copolymer may be the reason for its lower impact values. This effect is also reflected by the fact that only at a slightly greater block copolymer content (8% compared to 6%) the required domain distribution is achieved.

Tensile impact strength remains higher when compared to virgin PVC at rubber contents up to 10 wt% for all the blends. This shows that the heterogeneity of these systems is maintained at these compositions when the PU content of the rubber is low. Optimum dispersion and adhesion of rubber particles in the PVC matrix is the basic requirement of impact modification. At the lower levels of block copolymer contents, the PU hard segments of the lock copolymer provides only partial miscibility with PVC chains due to insufficient interaction providing optimum dispersion and adhesion of rubbery soft segment particles with the PVC phase. As a result of this, block copolymer forms a separate phase as domains which are kept dispersed in the PVC matrix. The domain configuration as confirmed by SEM studies discussed in a later section is ideal for the impact modification in these polymer blends.

The observed trend in impact strength of the present systems can be explained on basis of the theories of rubber toughening. Factors determining the toughening are the interfacial adhesion, the nature of the matrix, the nature of the rubber, the concentration of the rubber phase, and the shape and size of the rubber particles. Literature studies reveal that for effective toughening, the rubber particles should have an optimum size and must be uniformly distributed in the plastic matrix. Smaller and uniformly distributed particles are more effective in initiating crazes and in terminating them before they develop to catastrophic sizes [18].

Decrease in impact strength with composition in the case of blends with higher block copolymer content is attributed higher degree of compatibility to the level of miscibility due to the increased PU content in these samples. Evidence to this effect is provided by FTIR spectroscopic analysis, DSC studies, and tensile measurements.

In the light of these arguments it can be concluded that optimum level of phase adhesion and the optimum particle size needed for impact modification for the PVC/NR-*b*-PU$_3$ blend systems is achieved at 6 wt% block copolymer content. This corresponds to an optimum domain size of 0.96 μm and an optimum domain density of 8.72 × 10^{10} m $^{-2}$. These results were obtained from plots given in Figs. 4 and 5 which show the variation in tensile impact strength versus average domain size and domain density, respectively. The figures show that impact strength decreases in comparison with virgin PVC above the critical size 2.2 μm and critical domain

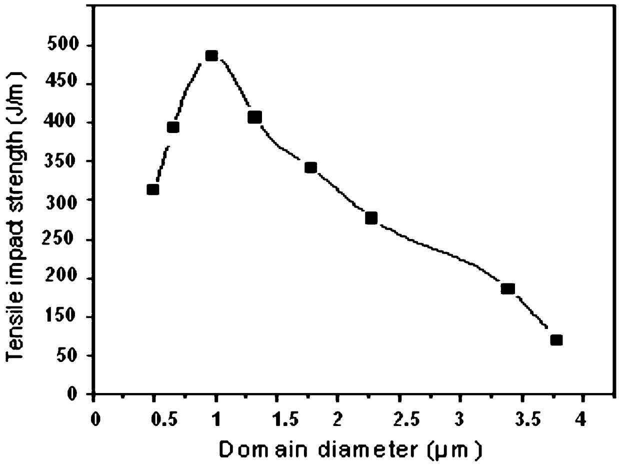

Fig. 4 Variation of tensile impact strength with domain density for PVC/NR-*b*-PU$_3$ blends

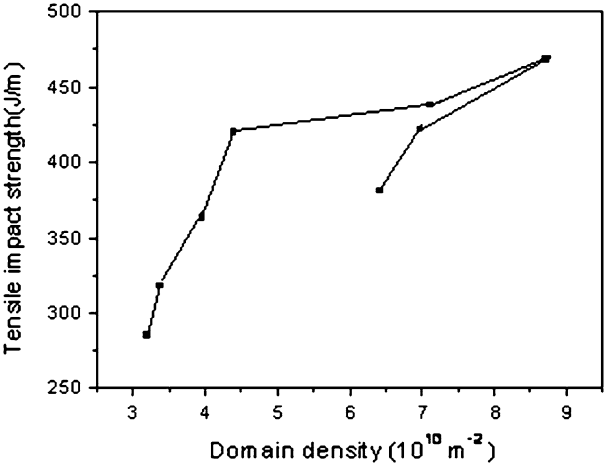

Fig. 5 Variation of tensile impact strength with average domain diameter for PVC/NR-*b*-PU$_3$ blends

Table 4 Domain size, domain size distribution, and domain density values of PVC/NR-*b*-PU_3 blends

Sample	Average domain size distribution (μm)	Average domain size (μm)		Domain density (m^{-2})
		D_n	D_w	
NR-*b*-PU_3 (98/2)	0.1–0.6	0.5	0.65	6.42×10^{10}
NR-*b*-PU_3 (96/4)	0.2–0.7	0.66	0.85	6.93×10^{10}
NR-*b*-PU_3 (94/6)	0.3–1	0.98	1.68	8.72×10^{10}
NR-*b*-PU_3 (92/8)	0.5–2	1.33	2.06	7.13×10^{10}
NR-*b*-PU_3 (90/10)	1–4	1.78	2.19	4.4×10^{10}
NR-*b*-PU_3 (80/20)	1.2–5	2.26	2.73	3.96×10^{10}
NR-*b*-PU_3 (70/30)	2–7	2.89	3.33	3.584×10^{10}
NR-*b*-PU_3 (60/40)	3–8	3.78	4.06	3.2×10^{10}
NR-*b*-PU_3 (50/50)	Co-continuous phase			
NR-*b*-PU_3 (30/70)	0.7–3	1.8	2.56	4.2×10^{10}

density 3.96×10^{10} m^{-2}. Reduction in tensile impact strength in samples with more than 20 wt% of the block copolymer is due to the presence of increased rubber content in them. The increased rubber content in these samples leads to a considerable reduction in tensile strength. This further decreases the tensile impact strength**.** Even though the phase adhesion is improved due to PVC–PU interactions, coalescence effect out weighs this leading to an increase in the particle size. Domain size of the block copolymer exceeds the critical size which explains the progressive decrease in impact properties. All these results are obtained from SEM analysis which is discussed in the next section.

The same arguments is valid for the other two series of blends also, viz., PVC/NR-*b*-PU_1 and PVC/NR-*b*-PU_2. Thus, the former is expected give optimum morphology at 6 wt% of the block copolymer and the latter is expected to give optimum morphology at 8 wt%.

SEM analysis of PVC/NR-*b*-PU blends

Since three blend systems are identical a representative series viz., PVC/NR-*b*-PU_3 is selected for morphological studies. SEM micrographs of PVC/NR-*b*-PU_3 (98/2), (96/4), (94/6), and (92/8) blends are shown in Fig. 6a, b, c, and d, respectively. The overall features such as scaling effect, etc., are almost same as that of PVC showing rigid nature. In the micrographs, a number of small circular patches are observed. These regions are supposed to be the micro-domains of the block copolymer dispersed in PVC matrix. As the block copolymer content progressively increases these domains gain in size.

Micrographs with 2 and 4% block copolymer are characterized by unevenly distributed micro-domains. Average domain size increases from 0.5 to 0.66 μm with a corresponding increase of domain density from 6.42×10^{10} to 6.93×10^{10} m^{-2}. Further addition of 2% block copolymer yielded a micrograph shown in Fig. 6c. Domain size increased to 0.98 μm with domain density value 8.72×10^{10} m^{-2} (Table 4). Coalescence of the block copolymer phase explains the increase in size.

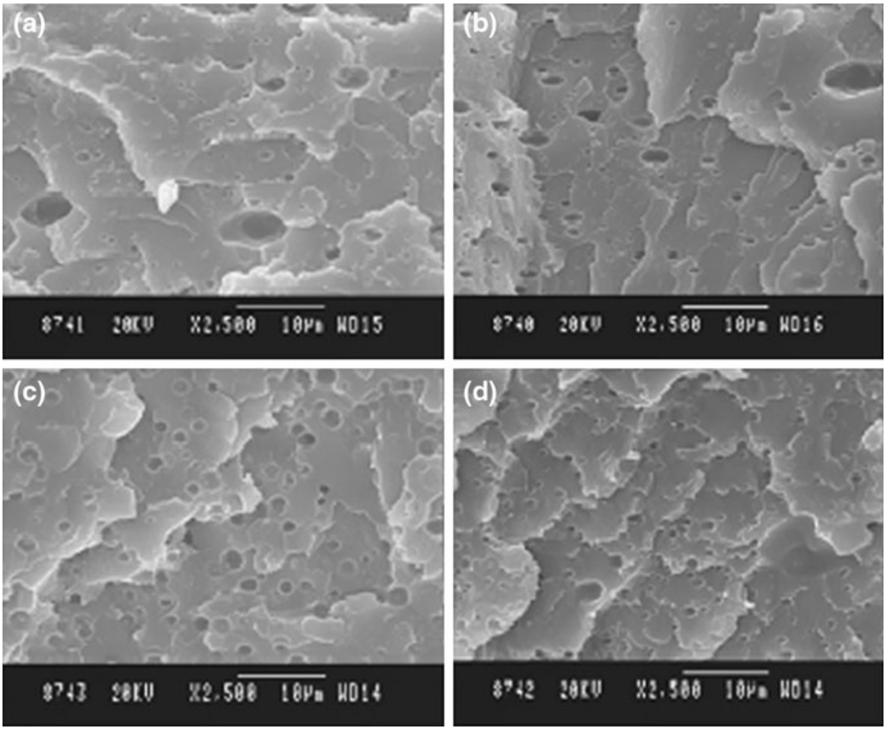

Fig. 6 Scanning electron micrographs of **a** 98/2, **b** 96/4, **c** 94/6, and **d** 92/8 compositions of PVC/NR-*b*-PU_3 blends

Above this at 8 wt% of block copolymer composition coalescence effects are pronounced which progressively increases the domain size and decreases the domain densities. Micrograph of this composition (Fig. 6d) showed a domain size of 1.33 μm and average domain density of 7.13×10^{10} m^{-2}.

SEM micrographs of samples with compositions (90/10), (80/20), (70/30), (60/40), (50/50), and (20/80) are shown in Fig. 7a, b, c, d, e, and f, respectively. The average domain size, size distribution, and the average domain density values are listed in Table 4. It is found that domain distribution increases to 3–8 μm and the average domain size increases to 3.78 μm up to 60/40 composition. The domain density, however, shows a decrease from 6.42×10^{10} m^{-2} to 3.2×10^{10} m^{-2} after reaching a maximum at (94/6) composition. Sample with (50/50) composition shows morphology with a co-continuous phase as shown in Fig. 7e. The micrograph shows the characteristics of a soft and a loose material. The micrograph of PVC/NR-*b*-PU_3 (20/80) blend (Fig. 7f) shows a matrix rich in soft block copolymer phase as seen by the ridges and the torn and wavy appearance of the fracture surface. It shows phase inversion in which PVC phase dispersed as domains in the block copolymer matrix. It can be seen from the morphological features of these blends that maximum domain densities is present up to 6 wt% of the block copolymer. This

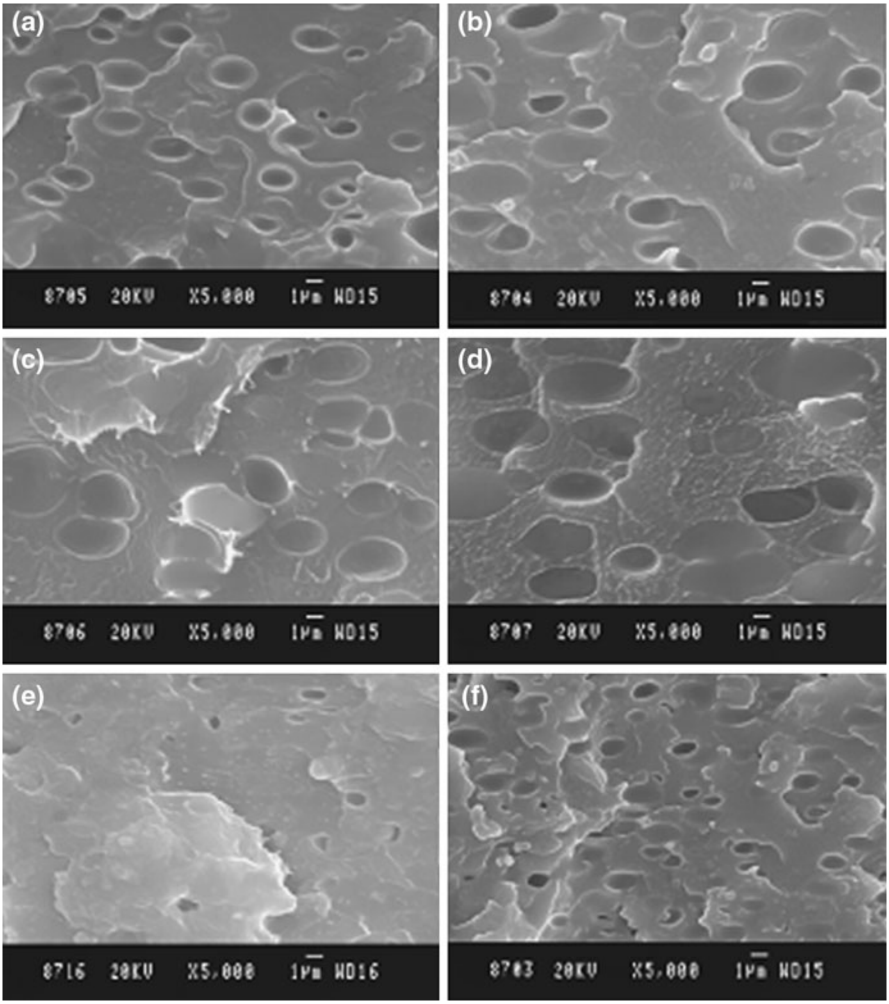

Fig. 7 Scanning electron micrographs of **a** 90/10, **b** 80/20, **c** 70/30, **d** 60/40, **e** 50/50, and **f** 20/80 compositions of PVC/NR-*b*-PU_3 blends

observation is in conjunction with the impact modification attained at this level of block copolymer concentration for this blend system.

Tensile impact fracture studies by SEM

The tensile impact fracture surfaces of PVC and selected samples of the blends were examined using SEM and the surface topology is related to the tensile impact properties. As in the previous studies NR-*b*-PU_3 blends are extensively studied and the results compared with selected samples of the other two series.

Tensile impact fracture surface of unmodified PVC is shown in Fig. 8a. The fracture surface has got a scaling pattern or a patch pattern which indicates a brittle

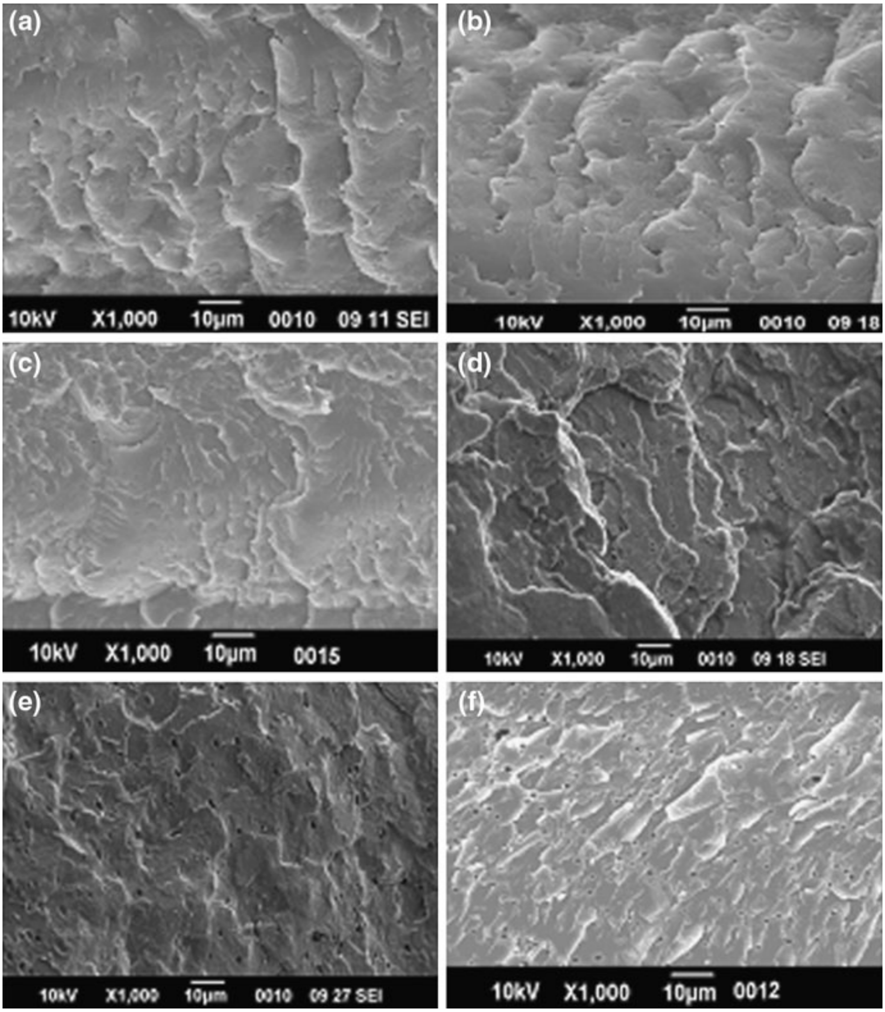

Fig. 8 The impact fracture surface of PVC/NR-*b*-PU$_3$ (98/2), (96/4), (94/6), and (92/8) and (90/10) compositions are given in **b**, **c**, **d**, and **e**, respectively

mode of fracture. This patch pattern is characteristic of fast crack growth from the initiation site which takes the shape of ridges during crack propagation in a direction away from the center of the crack.

The impact fracture surface of PVC/NR-*b*-PU$_3$ (98/2), (96/4), (94/6), (92/8), and (90/10) compositions are given in Fig. 8b, c, d, and e, respectively. All the micrographs show a plate-like rigid fracture with scaling effect indicating the rigid nature of the test samples. The impact fracture surface of PVC/NR-*b*-PU$_3$ (98/2) (Fig. 8b) is almost identical to that of PVC (Fig. 8a). With progressive addition of the block copolymer the appearance of the micrograph also changes. The scaling effect observed in unmodified PVC persists in the other compositions as seen in the micrographs of (94/6) and (96/4) compositions (Fig. 8c, d). The hard domain dispersions indicate that although fracture occurs as in a rigid material, the crack growth slows down with the presence of block copolymer domains. This factor must have contributed greatly to the impact strength of this system. Close examination of the micrographs reveals that the fracture surface becomes more and more deformed by the progressive addition of the block copolymer.

With the progressive addition of the block copolymer PU hard segments of the outer shell of the block copolymer interacts with PVC segments leading to formation of micro-dispersions of the block copolymer domains. PVC–PU interactions provide adhesion of the block copolymer domains with the PVC matrix. Block copolymer domains act as the centers of crack propagation due to the presence of its rubbery soft segment core. The essential requirement of semi-compatibility of the blend components together with heterogeneity of the blend components is achieved in all the three series of blends at lower compositions of the block copolymer. This is reflected in the higher value of impact strength obtained for the samples at 10 wt%, viz., 412, 402, and 420 J/m. Required domain morphology with appropriate domain size which is the essential requirement for impact modification is achieved at 6 wt% of the block copolymer for this blend series. Optimum level of compatibility and heterogeneity is achieved at this composition for this blend series which shows highest impact strength of 468 J/m.

The impact fracture surface of PVC/NR-*b*-PU_3 (90/10) is given in Fig. 9a. Micrograph shows scaling effect and a plate-like rigid fracture indicating the rigid

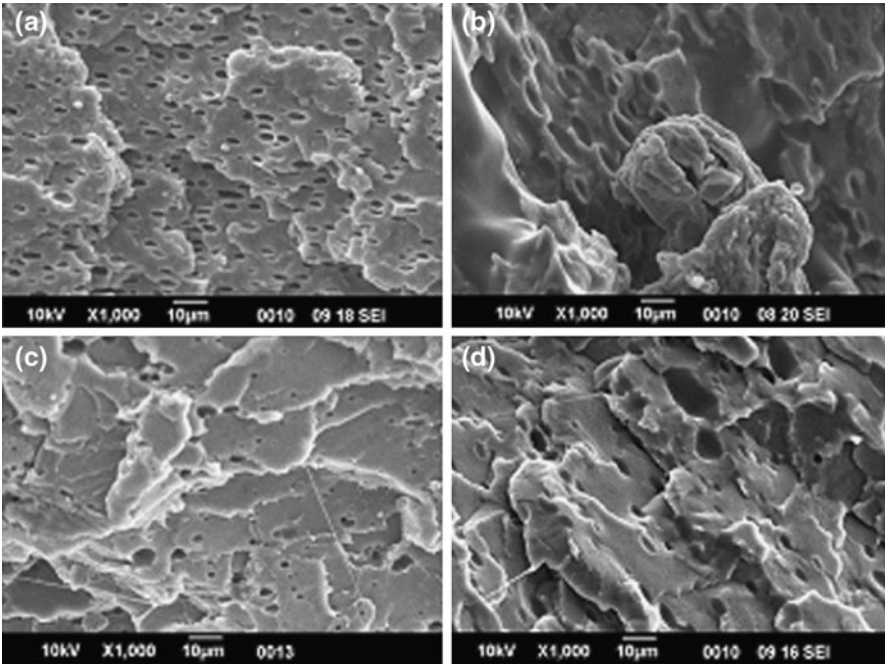

Fig. 9 Tensile impact fractographs of **a** PVC/NR-*b*-PU_3(90/10), **b** PVC/NR-*b*-PU_3(60/40), **c** PVC/NR-*b*-PU_2(90/10), and **d** PVC/NR-*b*-PU_2(60/40) blends

nature of the test sample. However, the patch pattern observed in unmodified PVC is less pronounced in this sample and the micrograph shows ridges indicating that although fracture occurs as in a rigid material, the crack growth slows down which follows a tearing mechanism. The impact fracture surface of PVC/NR-*b*-PU_3 (60/40) is shown in Fig. 9b. With 40% NR-*b*-PU_3 the surface is found to be deformed with ridges and pullout fragments. This appearance of the fracture surface is found to be characteristic of a soft material with more or less ductile behavior. Irregular patch pattern is observed on the fracture surface. It contains void which seems to be microcracks of $\sim$4 μm in length which are perpendicular to propagation of the fracture surface. These could be signs of localized flow deformation occurring during the fracture process. The transition from the brittle to a ductile behavior is in agreement with the variation in impact strength which however shows steady decrease with increase in block copolymer content. This decrease in impact strength may be caused by the rubber soft segment of the block copolymer in higher content to cause plastic deformation of the matrix. The other two series of blend samples of same composition also bears similar features as that of these blends as shown in Fig. 9c, d.

Conclusion

Blends of PVC and three different SPUs based on TDI with three different chain extender diols, viz., PG, 1,4-BDO, and 1,3-BDO have been prepared and characterized in terms of the impact properties. Optimum impact properties were shown at concentrations 6–8 % of the block copolymer. Based on these studies, NR-*b*-PU_3 seems to be the best candidate for imparting the highest impact strength to PVC followed by NR-*b*-PU_2. At these lower levels of block copolymer content, PU segments of the block copolymer provides partial miscibility with PVC due to insufficient intermolecular interaction. This leads to domain morphology for the samples. Optimum dispersion and adhesion of soft segment rubber particles with the PVC matrix explain the observed impact modification in these blends. At higher compositions there is deterioration in impact properties. Lowering of impact strength with higher block copolymer contents is an indication of excessive intermolecular interaction between the blend components leading to miscibility of the component polymers. The heterogeneous nature of the blend systems may be lost at this stage and plasticization of PVC matrix would take place. It is found that the impact modification is higher for NR-*b*-PU_3 blends when compared to the NR-*b*-PU_2 blends. High impact properties showed by these blends are attributed to the optimum level of compatibility achieved between the blend components. Tensile impact fracture studies revealed that failure pattern for these blend system transitioned from brittle to ductile fracture.

References

1. Zhu YQ, Huang YJ, Chi ZG (1995) The compatibility of the blends of PUs with PVC and the adhesion behavior of PU to PVC. J Appl Polym Sci 56:1371–1379

2. Sudaryanto TN, Nishino T, Ueno M, Asaoka S, Nakamae K (2001) Miscibility of segmented polyurethane/poly(vinyl chloride) blends. J Appl Polym Sci 82:3022–3029
3. Jaisankar SN, Anandprabu A, Lakshminarayana Y, Radhakrishnan G (2000) Preparation and properties of semi-interpenetrating polymer networks based on polyurethane ionomer/polyvinyl chloride. J Mater Sci 35:1065–1068
4. Petrovic ZS, Javni I, Shull J, Waddon A, Rubber J (1999) Chem Technol 72(4):587–593
5. Grigoreva OP, Stepanenko LV, Sergeeva LM (2002) Plasticization of polyvinyl chloride with reclaimed polyvinyl. Russ J Appl Chem 75(2):296–301
6. Manoj NR, Sivaraman P, Praveen S, Raut RD, Chandrasekhar L, Chakraborty BC (2005) Miscibility and fracture toughness of thermoplastic polyurethane/poly(vinyl chloride)/nitrile rubber ternary blends with special reference to the blend composition. J Appl Polym Sci 97(5):1763–1770
7. Grigoryeva O, Fainleib A, Stepanenko L, Sergeeva L (2005) Recycling of PVC/PU waste and reuse in PVC formulations: structure-property relationship. Polym Eng Sci 45(6):801–808
8. Parnell S, Min K (2005) Reactive blending of thermoplastic polyurethane in situ with poly(vinyl-chloride). Polym Eng Sci 45(6):876–887
9. Pielichowski K, Janowski B (2005) Semi-interpenetrating polymer networks of polyurethane and poly(vinyl chloride) Thermal stability assessment. J Therm Anal Calorim 80(1):147–151
10. Kim Y, Cho WJ, Ha CS (1999) Dynamic mechanical and morphological studies on the compatibility of plasticized PVC/thermoplastic polyurethane blends. J Appl Polym Sci 71(3):415–422
11. Ha CS, Kim Y, Lee WK, Cho WJ, Kim Y (1998) Fracture toughness and properties of plasticized PVC and thermoplastic polyurethane blends. Polymer 39(20):4765–4772
12. Xiao F, Deyan S, Zhang X, Hu S, Xu M (1987) Studies on the morphology of blends of poly(vinyl chloride) and segmented polyurethanes. Polymer 28(13):2335–2345
13. Karger-Kocsis J (1995) Polypropylene: structure, blends and composites. Chapman and Hall, London, p 2
14. Karian HG (1999) Handbook of polypropylene and polypropylene composites. Marcel Dekker, New York
15. Liang JZ, Li RKY (2000) Rubber toughening in polypropylene: a review. J Appl Polym Sci 77: 409–417
16. Ravindran T, Gopinathan Nair MR, Francis DJ (1986) A novel method for the preparation of hydroxyl terminated liquid natural rubber, Makromol. Chem Rapid Commun 7:159–163
17. Radhakrishnan Nair MN, Gopinathan Nair MR (2008) Synthesis and characterisation of soluble block copolymers from NR and TDI based polyurethanes. J Mater Sci 43:738–747
18. Yang D, Zhang B, Yang Y, Fang Z, Sun G, Feng Z (1984) Morphology and properties of blends of polypropylene with ethylene-propylene rubber. Polym Eng Sci 24:612–617