Investigation on Multiphase Polymeric Systems of Poly(vinyl Chloride). I. PVC–Chlororubber-20-*gp*-Styrene–Acrylonitrile (2 : 1) Blends

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Synopsis

A graft copolymer [chlororubber-20-*gp*-styrene–acrylonitrile (2 : 1)] has been synthesized by a solution precipitation polymerization technique grafting styrene and acrylonitrile onto chlororubber-20 main chain. The graft copolymer has been characterised by elemental analysis, IR spectroscopy, and viscometry. It has been blended with PVC by melt mixing using a Brabender plasticorder and extrusiograph. The mechanical properties such as flexural and tensile strengths and impact strength of the blends have been studied to evaluate its performance as an impact modifier. The behavior of PVC–chlororubber-20-*gp*-styrene–acrylonitrile (2 : 1) blends has also been compared with PVC–chlororubber-20 and PVC–KM-365B (a commercial acrylate modifier) blends. The thermal behavior of these blends has also been studied. It has been found that PVC–chlororubber-20-*gp*-styrene–acrylonitrile (2 : 1) blends have higher impact strength than PVC–chlororubber-20-*gp* blends though the PVC–KM-365B blends have the highest impact strength. Based on the authors' previous compatibility studies along with present X-ray diffraction studies and the morphological investigation of the fractured surface by scanning electron microscopy, the mechanical behavior of these blends have been explained in the framework of existing theories. A model has been proposed to account for the optimum dispersion and adhesion of graft polyblends of chlororubber-20 in PVC matrix.

INTRODUCTION

In last two decades, there has been tremendous growth in research activities on multiphase polymeric systems. Although new concepts for the development of new polymers have not been exhausted, either these new polymers never find any commercial use or they are used only for very special applications. However, for the large scale usage, the future belongs to the synergistic combinations of existing polymeric materials or multiphase polymeric systems. These materials are physical/chemical mixtures of structurally different polymers.[1]

The concept of the multiphase polymeric systems has mostly been used in the development of either impact resistance rigid plastics or reinforced rubbers and thermoplastic elastomers. In both the cases, the continuous phase

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retains most of its characteristic properties in the final product whereas the dispersed phase introduces certain unique properties in the system. In present study, poly(vinyl chloride) (PVC) has been chosen as the major component, and an attempt has been made to develop its blends having useful combination of various physical properties.

PVC is a brittle, hard, and semicrystalline polymer in its virgin state. It has many distinguished properties such as resistance to aging, good rigidity, reasonably high tensile strength, and high chemical resistance. However, PVC is a brittle polymer unless modified. Polymers of acrylonitrile, butadiene, and styrene (ABS), methyl methacrylate, butadiene, and styrene (MBS), copolymers of ethylene with vinyl acetate, and chlorinated polyethylenes are widely accepted as impact modifiers for PVC.[2]

Modified rubbers form a separate group of modifiers. However, all rubbers cannot be used because of their incompatibility with PVC matrix. In the present study, chlororubber-20 has been selected as backbone polymer, and styrene–acrylonitrile (2 : 1) has been grafted onto it to get suitable properties. The modifiers based on various chlororubbers have been very briefly reported in the literature.[3-5] Chloro derivatives of isobutylene–isoprene,[3] methyl methacrylate–styrene graft polyblends of polychloroprene,[4] and chloroprene rubbers[5] in combination with methyl methacrylate, α-methyl styrene have been used as modifiers for PVC.

The compatibility of component polymers is the fundamental problem in the studies of multiphase polymeric systems. In a successful blend system, component polymers retain most of their individual properties while having synergistic effects on other properties. The present system, i.e., PVC–chlororubber-20-*gp*-styrene–acrylonitrile (2 : 1) has been studied for its compatibility by a method developed in authors' laboratory and by other conventional methods.[6-11] The thermal behavior and stability have also been studied in details by the authors.[12,13]

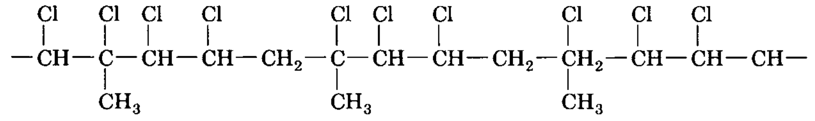
This paper describes the synthesis and characterization of chlororubber-20-*gp*-styrene–acrylonitrile (2 : 1) [CR-20-*gp*-SAN (2 : 1)] as well as the preparation of the blends by melt mixing using a Brabender plasticorder and extrusiograph. The mechanical properties have been studied to evaluate its performance as an impact modifier. The deformation behavior of the PVC blends has also been studied by scanning electron microscopy of their impact fractured surfaces. The present paper reports the results of these studies in detail.

EXPERIMENTAL

Materials

Poly(vinyl Chloride). PVC of powder grade (Shriram Chemicals, Kota, India, SR-10, K value = 65) was used for the preparation of blends.

Chlororubber-20. A powder grade chlororubber-20 (Rishiroop Polymers Ltd., Bombay, India) has been used. The material was purified by dissolution in methyl ethyl ketone followed by precipitation in excess methanol (L. R., BDH, India). The precipitation was carried out twice, and the product was vacuum-dried. Chlororubber-20 contains 55.4% chlorine according to gravimetric analysis after an exhaustive oxidation by Na_2O_2. Chlororubber-20 is an industrial product which is synthesized by the chlorination of polyisoprene rubbers. The exact chemical nature of the product is not revealed by the manufacturer. However, the most probable structure may be as follows:



$$-\overset{Cl}{CH}-\underset{CH_3}{\overset{Cl}{C}}-\overset{Cl}{CH}-\overset{Cl}{CH}-CH_2-\underset{CH_3}{\overset{Cl}{C}}-\overset{Cl}{CH}-\overset{Cl}{CH}-CH_2-\underset{CH_3}{\overset{Cl}{CH_2}}-\overset{Cl}{CH}-\overset{Cl}{CH}-CH-$$

The chlorine content varies according to the extent of chlorination. The presence of residual unsaturation [(C—C—Cl)] has also been reported.[14]

Styrene, and Aerylonitrile. Styrene-(Buragoyne Urbidges & Co., Bombay, India) and acrylonitrile (S.D.'s Chemicals, Bombay, India) monomers were purified by removing their inhibitors prior to their use. Solvents xylene (BDH, India), methyl ethyl ketone (MEK), (E. Merk, India), chloroform (BDH, India), methanol (BDH, India), isopropanol (SD's Chemicals Bombay, India), and tetrahydrofuran (E. Merk, India) were mainly of AR grades. Benzoyl peroxide (AR grade, BDH, India) was recrystallized from chloroform prior to its use. KM-365B (a commercial impact modifier for PVC; Indofil Chemicals, Bombay, India), barium cadmium laurate (thermal stabilizer, Amrut Chemicals Pvt. Ltd., Bombay, India), dioctyl phthalate (DOP) (plasticizer, Amrut Chemicals Pvt. Ltd., Bombay, India), and poly(methyl methacrylate) (PMMA) [processing aid, (BDH, U.K.), MW = 1×10^6] have been used in their original form.

Synthesis of Chlororubber-20-*gp*-Styrene–Acrylonitrile (2 : 1)

The styrene–acrylonitrile (SAN) graft polyblends reported in this paper were synthesized by a solution–precipitation polymerization technique.[15,16]

The synthesis was conducted in a reaction kettle equipped with an N_2 gas inlet tube, thermometer pocket, condenser, and mercury sealed mechanical stirrer. The temperature was controlled by a water bath in which this whole assembly was placed (Fig. 1).

The purified solvents and monomers were dried and were placed under N_2 atmosphere prior to their use. Fifty grams of purified CR-20 was dissolved in 400 mL xylene; 33.6 g of styrene and 16.7 g of acrylonitrile were added to xylene solution. In this process, a continuous stream of N_2 was flushed through the solution along with continuous stirring. After this, 0.89 g of benzoyl peroxide was added to the reaction mixture. The reaction mixture was heated at $80 \pm 1°C$, and reaction was carried out for 15 h. During this process, an inert atmosphere has been maintained by continuous flow of N_2 gas through reaction mixture. The continuous slow mixing was maintained by mechanical stirrer.

As the reaction proceeds, the level of conversion could be judged by observing the increasing turbidity of the reaction mixture which changes from yellowish grey to yellowish milky. During polymerization process, the temperature of reaction mixture has been raised by 7–8°C. Finally, after the completion of the reaction, the reaction product was recovered by precipitation in excess of methanol.

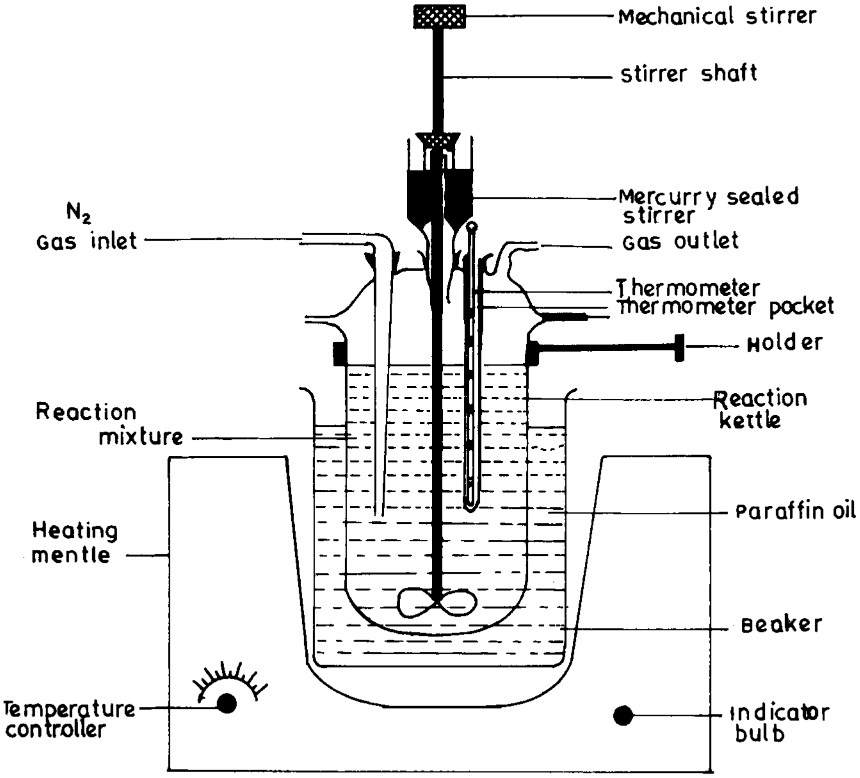


Fig. 1. Experimental set up for synthesis of graft polyblends of chlororubber-20.

Separation of Chlororubber-20-*gp*-Styrene–Acrylonitrile (2 : 1)

The content of the reaction mixture was cooled to the room temperature and poured in small quantities into an excess of methanol. The product, slightly yellowish rubbery powder, was dried at 60°C under vacuum for 48 h. The resulting yield was approximately equal to 90%.

The powder was dissolved in MEK and reprecipitated with methanol. The homopolymers of grafted components, i.e., polystyrene and polyacrylonitrile, and their possible copolymers were further separated from the crude reaction mixture by fractional reprecipitation from their MEK solutions by addition of isopropyl alcohol, a technique reported by Rao and Santappa[17] and Kaleem et al.[14] on the basis of Smets' work.[18] The product was dissolved in MEK and isopropyl alcohol (volume fraction, $\gamma = 0.25$) was added into solution. This process has been repeated thrice. A model experiment (Table I) was carried out on the mixture of CR-20 with polystyrene. Homopolymer recovery was equal to approximately 98%. The product obtained was used in further studies.

Grafting Percentage and Grafting Efficiency

No suitable solvent could be found for the selective elution of backbone polymer from the reaction product. Apparent grafting percentage and grafting

TABLE I
Model Experiments of Separation of Component Polymers from CR-20/Polystyrene Mixtures

	Entry no. 1	Entry no. 2
Charged Quantity:		
CR-20	1.000 g, 50%	1.5 g, 75%
Polystyrene	1.000 g, 50%	0.5 g, 25%
Recovered amount:		
process—dissolved in MEK and precipitated by isopropyl alcohol ($\gamma = 0.25$); process repeated for three times		
CR-20	1.045 g, 50.85%	1.548 g, 75.20%
Polystyrene	1.010 g, 49.15%	0.508 g, 24.80%

efficiency have thus been determined from the following expressions:

$$\text{apparent grafting percentage} = \frac{\text{wt grafted segment}}{\text{wt backbone polymer}} \times 100$$

$$\text{apparent grafting efficiency} = \frac{\text{wt grafted segment}}{\text{wt grafted segments} + \text{wt homopolymers}} \times 100$$

These quantities were calculated on the basis of gravimetric measurements. Since monomer mixtue was used for grafting purpose, the weight of grafted segments represents the total weight of the grafted components. Grafted branches of the monomers were randomly placed onto backbone polymers; therefore, the grafted content was considered in percentage G. E. and percentage grafting calculations.

Characterization

Elemental Analysis

Carbon, hydrogen analyses were performed by Thomas CH Analyser, 35 Carbo Erba 1106 whereas nitrogen analysis was performed by Coleman N-analyser-29.

Intrinsic Viscosity

Intrinsic viscosity of chlororubber-20 and its graft polyblend was measured by a Ubbelohde viscometer at 23.3°C using chloroform as solvent. Viscometric average molecular weight was calculated on the basis of earlier reported data for chlororubber.[17]

Infrared Spectroscopic Analysis

Infrared measurements were made on a Perkin-Elmer infrared spectrophotometer using Nujol as solvent.

TABLE II
The Formulation Receipe for PVC Blends

Materials	Quantity by weight
PVC (SR-10, F = 65)	100 parts
Ba–Cd laurate	2 parts
Dioctyl phthalate	8 parts
Procesing aid (PMMA)	1.5 parts
Titanium oxide	8 parts
Modifiers	X percentage[a]

[a] X = the weight percentage of various modifiers, in the range of 0–25%.

Mechanical Properties of PVC–Chlororubber-20-*gp*-Styrene–Acrylonitrile (2 : 1) Blends

Formulation

Formulations were prepared in accordance to a standard compounding recipe[19] (Table II).

Processing

The above-mentioned formulations of PVC were mixed in powder form by an ordinary mixer. These mixed powder formulations have been further mixed and extruded by a Brabander plasticorder and extrusiograph at 150–165°C. The temperatures of various heaters of the extruder were fixed in the following orders: first heater, 150°C; second heater, 155°C; third heater, 160°C; fourth heater, 165°C. A 2-mm diameter die has been used for extrusion and its temperature has been fixed at 165°C. The rate of mixing was maintained almost the same for each formulation. The extruded material was obtained in the form of cylindrical strands, and the strands have been cut into regular small cylindrical pellets by a pelletizer.

The cylindrical pellets have been molded into sheet form by a compression molding technique. The small-sized cylindrical pellets were appropriately stacked in a mild steel case (8 × 8 × 0.33 cm) in between two thin polished stainless steel sheets (1 mm thickness) and molded at 150 ± 1°C for 3 min at 60 kg/cm^2 pressure as per operations depicted in Table III.

TABLE III
Compression Molding of PVC Blends

Sample no.	Operation	Temp (°C)	Pressure	Time (min)
1	Contacting of upper and lower plateform of hydraulic press	150	Atmospheric	0.5
2	Contact under pressure	150	10 kg/cm^2	1
3	Molding operation	150	60 kg/cm^2	1.5

The specimens for various testings were cut and machined from the prepared sheet. The tests samples were conditioned according to ASTM standard[20] prior to their testing and were annealed at 72°C for 48 h.

Testing Procedure

Flexural Strength

The flexural strength and moduli of PVC blends were measured by three-point bending using universal testing machine (Model FU 10000, GDR) at the strain rate of 5 mm/min.

Tensile Testing

The stress–strain measurements have been made in tension by using an Instron testing machine at 1 cm/min strain rate and at 23.8°C.

Impact Strength

PVC blend samples were tested for their impact strength using the Avery Izod impact testing machine no. 6702 (a commercial machine). The samples were tested according to the ASTM-D 256-56A method.

Fracture Surface Analysis by Scanning Electron Microscopy

The surface of fractured specimens have been studied by scanning electron microscope (IST-60). The fractured surface was coated with copper by the vacuum evaporation technique prior to its study.

X-Ray Diffraction Analysis of PVC Blends

X-ray diffraction measurements were carried out by monitoring an X-ray diffraction pattern between 10 and 35° Bragg angles at the scanning rate of 2°/min by an X-ray diffractometer (Model DRON-1, USSR) using Ni-filtered CuKα radiation.

RESULTS AND DISCUSSION

Synthesis and Characterization of Chlororubber-20-*gp*-Styrene–Acrylonitrile (2 : 1)

The results of separation are displayed in Table IV.

The isolated graft polymer containing some amount of ungrafted CR-20 was used in further studies, i.e., studies on compatibility, mechanical and thermal

TABLE IV
Separation of CR-20-*gp*-SAN (2 : 1) from Reaction Product

Charged quantity of product: 90.78 g	
Recovery by refractionation process	
Polystyrene homopolymer	5.55 g, 6.1%
CR-20-*gp*-SAN (2 : 1)	85.23 g, 93.9%

TABLE V
The Results of Elemental and Viscometric Analyses of CR-20-*gp*-SAN (2 : 1)

Elemental analysis	Carbon	55.8%
	Hydrogen	5.74%
	Nitrogen	3.03%
	Oxygen[a]	Negligible
	Chlorine	35.93%
Composition of graft polyblend	Chlororubber-20	65.85%
	Polystyrene	23.67%
	Polyacrylonitrile	11.47%
Intrinsic viscosity		0.250
Percentage grafting efficiency[b]		59.92
Grafting percentage		54.19
Grafting efficiency		85.57

[a] Value excluding oxygen of H_2O.

[b] Apparent value, i.e., % G. E. = [(weight of grafted monomer)/(total weight of monomer added)] × 100.

properties. No suitable solvent for separation of backbone polymer could be found after a long trial of various solvents.

As the objective has been to prepare polymer in bulk quantity for various studies, the grafting efficiency and percentage grafting has been calculated in the above-stated reaction conditions only. Since more than one monomer have been grafted, the monomers have been considered as one entity, and the grafting efficiency was calculated considering the total grafted content of the components. Table V shows the results of elemental and viscometric analyses of graft polyblend of styrene and acrylonitrile.

It has already been established that grafting reactions of chlororubber are chain transfer reactions,[17,21] in which a growing macromolecular radical is transferred to the backbone polymer. The chain transfer is facilitated by the presence of chlorine in the backbone polymer.[17,21] Thus, the macromolecular radical transfer would be dependent upon its compatibility with the backbone or graft copolymer. The effect would be very small since the polymerizing medium, xylene, provides all opportunities to every growing chain to get in the proximity of backbone or graft polymer. However, more compatible macromolecular radicals would have higher access to the chain transfer site than comparatively less compatible components. The point has been strengthened when GE and GP of graft polyblends of various other monomer mixtures have been compared.[9-11]

The grafting has been established by the following observations:

1. Detecting a weight increase in the final grafted product over that of the charged chlororubber-20.
2. From elemental analysis, the presence of nitrogen is indicative of PAN component in the grafted polymers. Nitrogen is almost absent in CR-20.
3. The grafting of styrene and acrylonitrile is evident from the infrared spectra of isolated graft polyblend and chlororubber-20. Figures 2 and 3 show the infrared spectrum of chlororubber-20 and its graft polyblend, i.e., CR-20-*gp*-SAN (2 : 1). The following results may be inferred from this analysis.

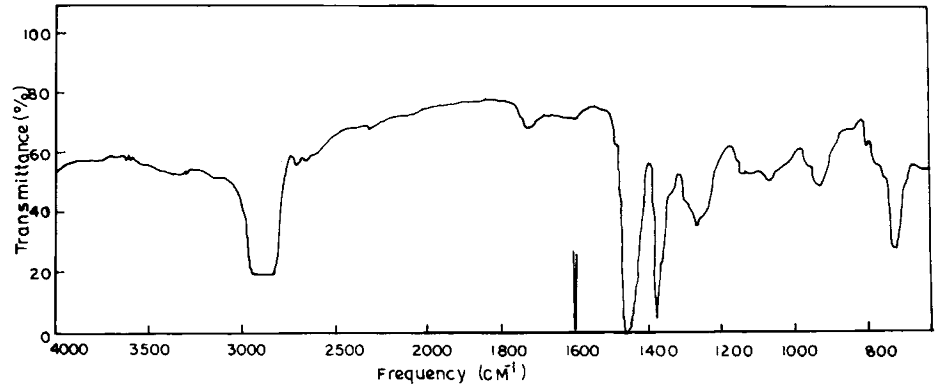


Fig. 2. Infrared spectra of chlororubber-20.

The characteristic band of monosubstituted aromatic ring at 700–705, 1030, 1070, 1480, 1600, and 1575 cm^{-1} in the infrared spectrum of CR-20-*gp*-SAN (2 : 1) indicates the presence of polystyrene chains at the backbone polymers (Fig. 3). Furthermore, a strong band characteristic of the —CN group at 2210–2225 cm^{-1} from the same sample is indicative of PAN grafted chains (Fig. 3). The absence of above-mentioned infrared absorption band in CR-20 (Fig. 2) also establishes grafting.

The differential thermograms of CR-20 and its graft polyblend, CR-20-*gp*-SAN (2 : 1), have been given in Figure 3 of Ref. 9. The glass transition temperature of CR-20 and its graft polyblend could not be obtained since DTA was performed above room temperature while their T_g's are expected below room temperature (T_g of CR-20 = −40°C). However, it may be inferred from various thermograms that the exothermic nature of CR-20 degradation is subdued by the introduction of grafted polymeric components in its matrix. Furthermore, the T_g of polystyrene component is exhibited in the thermogram. Although the transition is broad and weak, it is significant enough to predict the presence of polystyrene component in the graft polymer. The broad and weak nature of transition is also indicative of the graft copolymer.

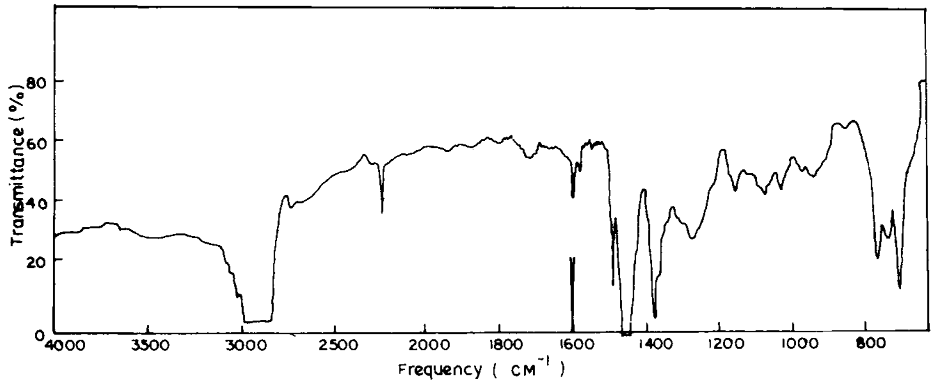


Fig. 3. Infrared spectra of chlororubber-20-*gp*-styrene–acrylonitrile (2 : 1).

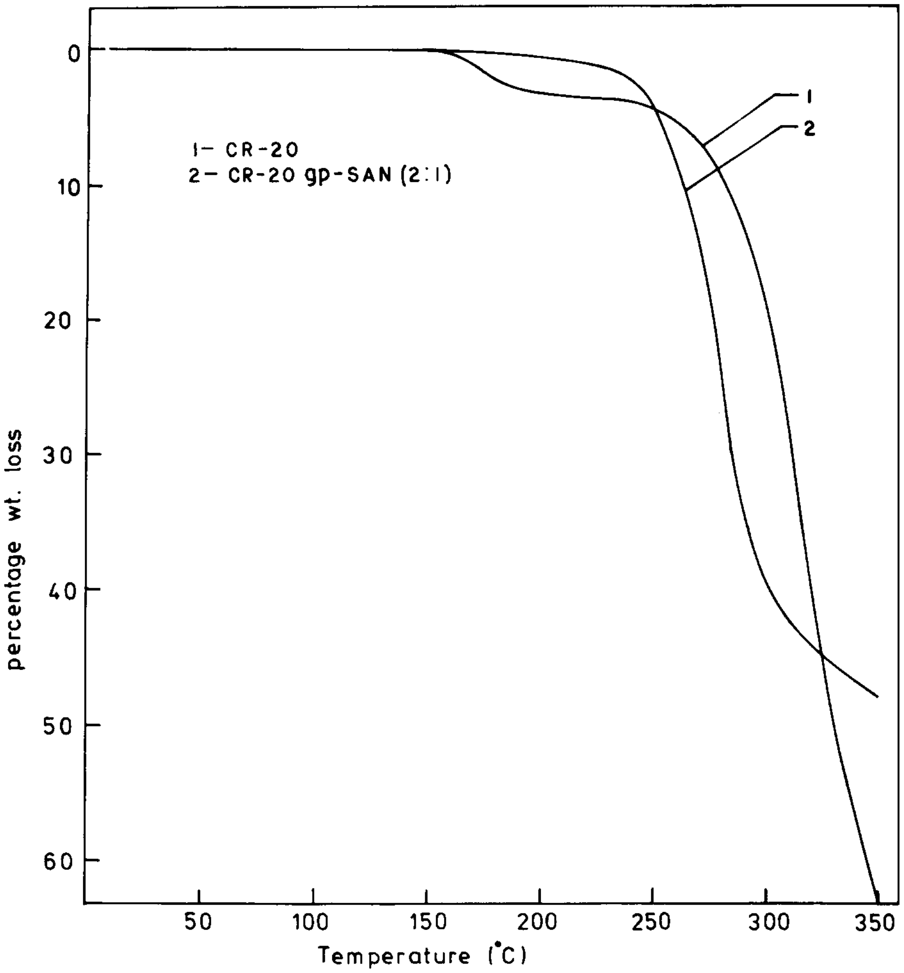


Fig. 4. Percentage weight loss vs. temperature of chlororubber-20 (1) and its graft polyblends (2) [CR-20-*gp*-SAN (2 : 1)] in nitrogen atmosphere.

The T_g corresponding to PAN could not be detected because it is above the decomposition temperature of polymer itself.

The results of thermogravimetric analysis of graft polyblend and CR-20 have been shown in Figures 4, 5, and 6. It may be analyzed from these thermograms that the grafting of SAN polymeric components onto CR-20 backbone introduces certain amount of thermal stability to main chain. CR-20 starts degrading at comparatively lower temperature in comparison to its graft copolymers. The higher thermal stability of CR-20-*gp*-SAN (2 : 1) at the initial portion of the high temperature range in comparison to CR-20 may be attributed to the stabilizing action of the polystyrene component. The effect is similar to that of the effect of polystyrene on PVC matrix.[22,23] The graft polyblend shows a tendency of further improvement in thermal stability at higher temperatures (> 300°C), which is indicative of effective thermal stabilization by polystyrene at higher temperature as has been noticed by Dodson et al.[24] in PVC–polystyrene blends. The role of various components in

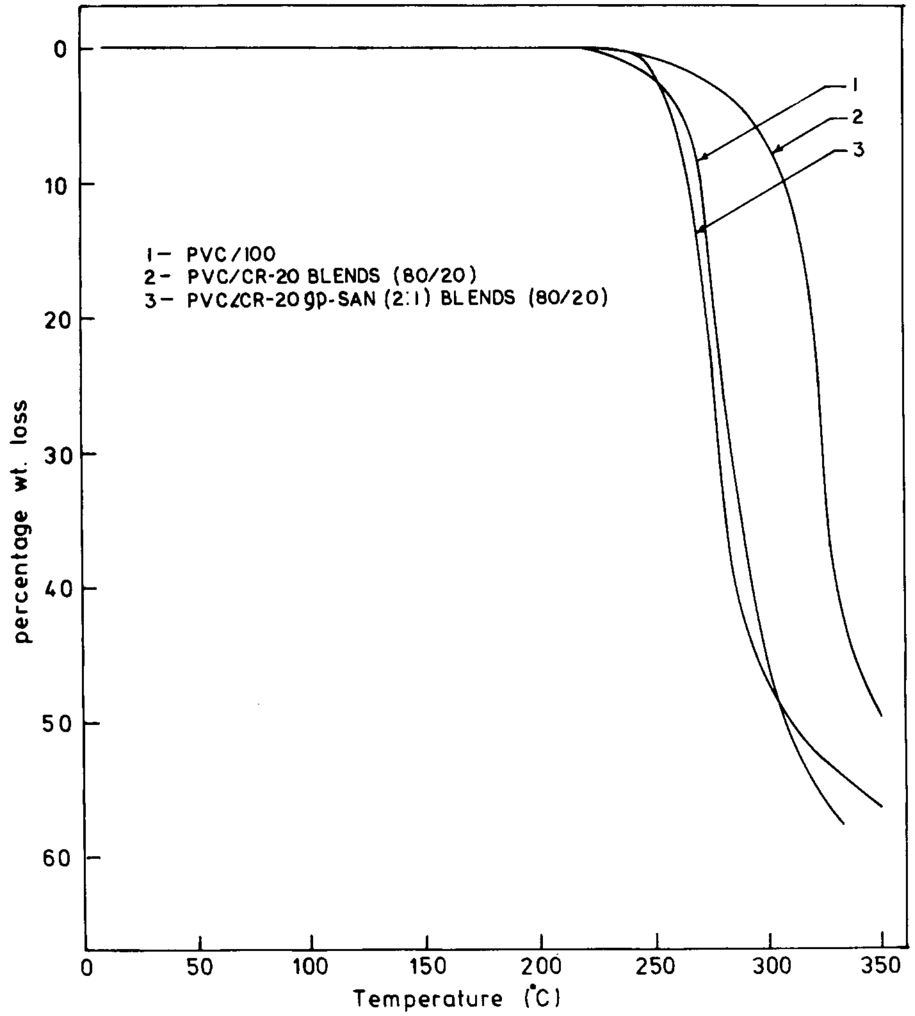


Fig. 5. Percentage weight loss vs. temperature of various PVC blends in nitrogen atmosphere: (1) PVC (100); (2) PVC/CR-20 blends (80/20); (3) PVC/CR-20-*gp*-SAN (2 : 1) blends (80/20).

stabilization and destabilization of the CR-20 phase has been extensively discussed recently.[11-13,23] It has been observed that the induction time of degradation (the time taken by the blend for initiation of degradation at a constant temperature) is of the following order for various blends:

PVC–KM-365B > unmodified PVC > PVC–CR-20-*gp*-SAN (2 : 1)

> PVC–CR-20

The unmodified PVC is found to be more stable than CR-20 and CR-20-*gp*-SAN (2 : 1). It may be due to the destabilizing effect of their decomposition products HCl and NH_3 which catalyze the degradation reaction of PVC. The PVC–CR-20-*gp*-SAN (2 : 1) blends are found to be more stable than the PVC–CR-20 blends due to the stabilizing effect of the polystyrene phase on the PVC matrix, as has been discussed by McNeill et al. for PVC–PS

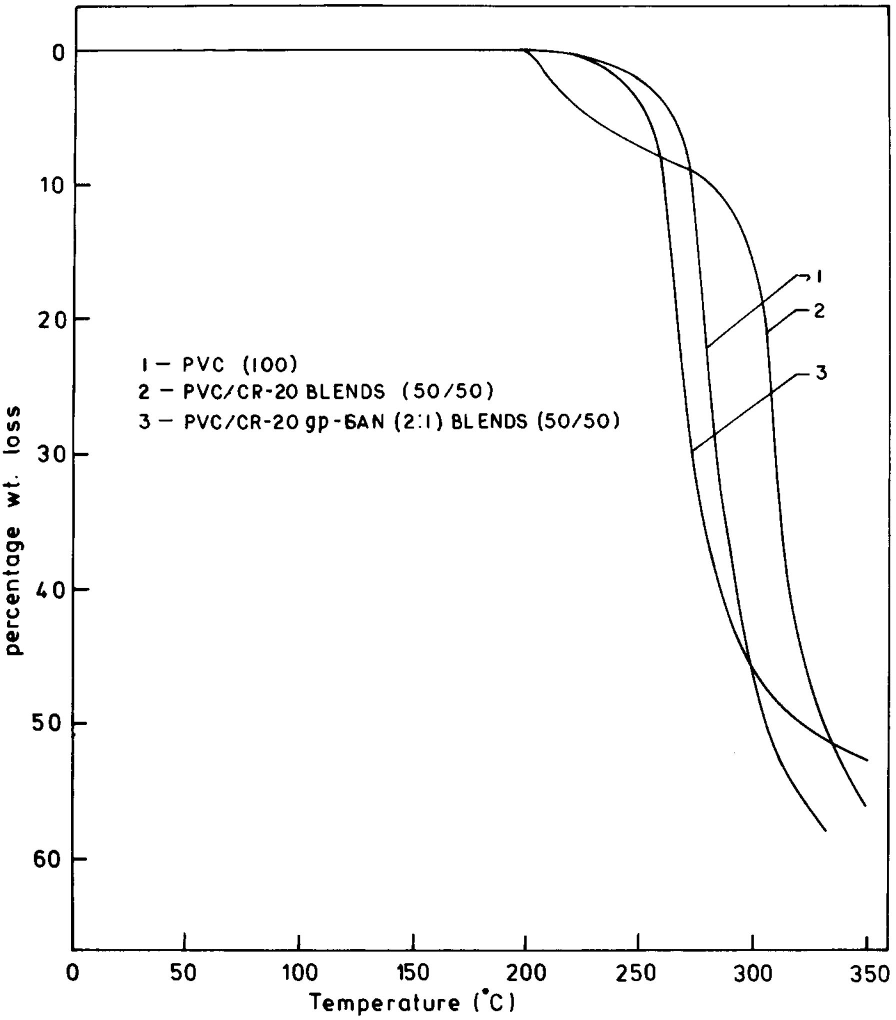


Fig. 6. Percentage weight loss vs. temperature of various PVC blends in nitrogen atmosphere: (1) PVC (100); (2) PVC/CR-20 blends (50/50); (3) PVC/CR-20-*gp*-SAN (2 : 1) blends (50/50).

blends.[22,24,25] The stabilizing action of the acrylate phase by following two processes makes PVC–KM-365B more stable than unmodified PVC. First, when chlorine radicals from the PVC dehydrochlorination site enter the polyacrylate phase and initiate the depolymerization which may compete with PVC for chlorine radicals, the evolution of HCl in reduced. Secondly, the interaction of the HCl with ester group of acrylate phase results in the formation of anhydride rings in the polymer chains which may block further degradation.

The authors have studied the compatibility of PVC–CR-20 and PVC–CR-20-*gp*-styrene–acrylonitrile (2 : 1) blends extensively by thermal analysis, ultrasonic, and viscometric methods.[9,10,13] It has been observed that CR-20 makes compatible blends with PVC, which may have traces of microheterogeneity. This observation is in conformity with the observations made by

Friese[26] for PVC–chlororubber blends. The PVC–CR-20-*gp*-SAN (2 : 1) blend system is also found to be incompatible system. The heterogeneity is more prominent at higher concentrations of PVC. The PVC forms incompatible blends with polystyrene.[27,28] In the complex molecule of CR-20-*gp*-SAN (2 : 1), polystyrene and PAN chains are grafted onto CR-20 backbone when PVC and CR-20-*gp*-SAN (2 : 1) are blended; the CR-20 molecules act as compatibilizing agent. The concentrations of CR-20, polystyrene, and PAN play a decisive role in compatibility behavior. At higher concentrations of PVC, the incompatible character of polystyrene and PAN groups dominate over the compatible nature of the CR-20 backbone, resulting in incompatibility of blends.

Mechanical Properties of PVC–Chlororubber-20-*gp*-Styrene–Acrylonitrile (2 : 1) Blends

As mentioned earlier, PVC has low impact stength. An attempt has been made to improve its impact strength by incorporation of chlororubber-20 and its graft polymers in PVC matrix. The performance of chlororubber-20-based

TABLE VI
Mechanical Properties of PVC–CR-20 Blends

Sample no.	Weight percentage of modifier	Bulk density (g/cm^3)	Izod impact strength (kg cm/cm) of notch	Flexural strength (kg/cm^2 × 10^{-2})	Flexural modulus (kg/cm^2 × 10^{-3})	Tensile strength (kg/cm^2 × 10^{-2})
1	0	1.3609	3.75	7.50	14.75	3.97
2	5.0	1.5615	3.70	7.57	13.25	4.12
3	10.0	1.5600	5.29	7.25	12.65	3.65
4	12.5	1.5602	6.54	7.02	11.75	3.04
5	15.0	1.5235	5.25	5.73	—	2.60
6	17.5	1.5268	3.74	4.93	9.25	—
7	20.0	1.4442	3.30	3.94	8.20	2.35
8	25.0	1.5673	2.30	3.25	7.28	1.97

TABLE VII
Mechanical Properties of PVC–CR-20-*gp*-SAN (2 : 1) Blends

Sample no.	Weight percentage of modifier	Bulk density (g/cm^3)	Izod impact strength (kg cm/cm) of notch	Flexural strength (kg/cm^2 × 10^{-2})	Flexural modulus (kg/cm^2 × 10^{-3})	Tensile strength (kg/cm^2 × 10^{-2})
1	0	1.3609	3.75	7.50	14.50	3.97
2	5.0	1.2488	3.80	7.60	14.40	3.72
3	10.0	1.3367	7.50	7.48	14.25	3.90
4	12.5	1.3585	7.87	7.00	13.50	—
5	15.0	1.4353	6.72	6.00	12.98	3.42
6	17.5	1.4235	4.27	—	—	—
7	20.0	1.4195	2.42	4.43	9.50	1.86
8	25.0	1.4143	2.00	3.50	8.03	0.96

TABLE VIII
Mechanical Properties of PVC–KM-365B Blends

Sample no.	Weight percentage of modifier	Bulk density (g/cm^3)	Izod impact strength (kg cm/cm) of notch	Flexural strength (kg/cm^2 × 10^{-2})	Flexural modulus (kg/cm^2 × 10^{-3})	Tensile strength (kg/cm^2 × 10^{-2})
1	0	1.3609	5.75	7.50	14.75	3.97
2	5.0	1.5647	3.90	7.25	13.76	3.42
3	10.0	1.5207	6.75	7.00	13.40	3.30
4	12.5	1.4511	—	—	—	—
5	15.0	1.4616	7.90	6.50	12.97	2.29
6	17.5	1.4495	5.02	6.32	—	2.23
7	20.0	1.4760	3.27	6.41	—	2.10
8	25.0	1.4462	2.50	5.38	12.00	2.02

modifiers has been compared with that of the commercial modifier KM-365B. The CR-20-based modifiers contain approximately 35% of total grafted polymeric components. Modifier's efficiency is a critical criterion for comparing the performance of the modifiers. It is the relative ability of the modifiers to impart impact strength to PVC at low modifier concentrations.

The blends of PVC with various modifiers were prepared at various modifiers concentrations, viz., 5, 10, 12.5, 15, 20, and 25%. The physical properties of these blends have been compared to those of the unmodified PVC. Furthermore, the performance of these blends has also been discussed comparatively. The results of various mechanical properties are listed in Tables VI–VIII. Critical values are further summarized in Table IX.

Flexural Strength and Modulus

In the present study, chlororubber-20 has been used as a base material to be blended with PVC. The rest of the modifiers have been developed by grafting the mixtures of various monomers onto the chlororubber-20 backbone chain. Various studies show that the monomer mixtures of 2 : 1 ratio result in the most desirable materials for impact modification of PVC.[29–31] Hence the compositions mentioned have been undertaken into consideration. The flexural properties of PVC blends have been depicted as a function of the concentration of modifiers. Tables VI and VII and Figure 7 depict various results of flexural properties. The following observations have been made from the analysis of the data.

1. The incorporation of various modifiers results in the reduction of flexural strength. The flexural strength of the blends either remains constant or increases marginally at lower concentrations of modifiers (generally up to 10%).
2. The comparative account of flexural strength shows that the overall performance of PVC–CR-20-*gp*-SAN (2 : 1) blends has been better than PVC–CR-20 blends. The following trend of flexural strength was observed

TABLE IX
Mechanical Properties of PVC Blends

Sample no.	System	Weight percent-age of modifier	Bulk density (g/cm^3)	Izod impact strength (kg cm/cm) of notch	Flexural strength (kg/cm^2 × 10^{-2})	Flexural modulus (kg/cm^2 × 10^{-3})	Tensile strength (kg/cm^2 × 10^{-2})
1	PVC–CR-20 blends	10.0	1.5600	5.29	7.25	12.65	3.65
		12.5	1.5602	6.54	7.02	11.75	3.04
		15.0	1.5235	5.25	5.73	—	2.60
2	PVC–CR-20-*gp*-SAN (2 : 1) blends	10.0	1.3367	7.50	7.48	14.25	3.90
		12.5	1.3585	7.87	7.00	13.50	—
		15.0	1.4353	6.72	6.00	12.98	3.42
3	PVC–KM-365B blends	10.0	1.5207	6.75	7.00	13.48	3.30
		12.5	1.4511	—	—	—	—
		15.0	1.4616	7.90	6.50	12.97	2.29

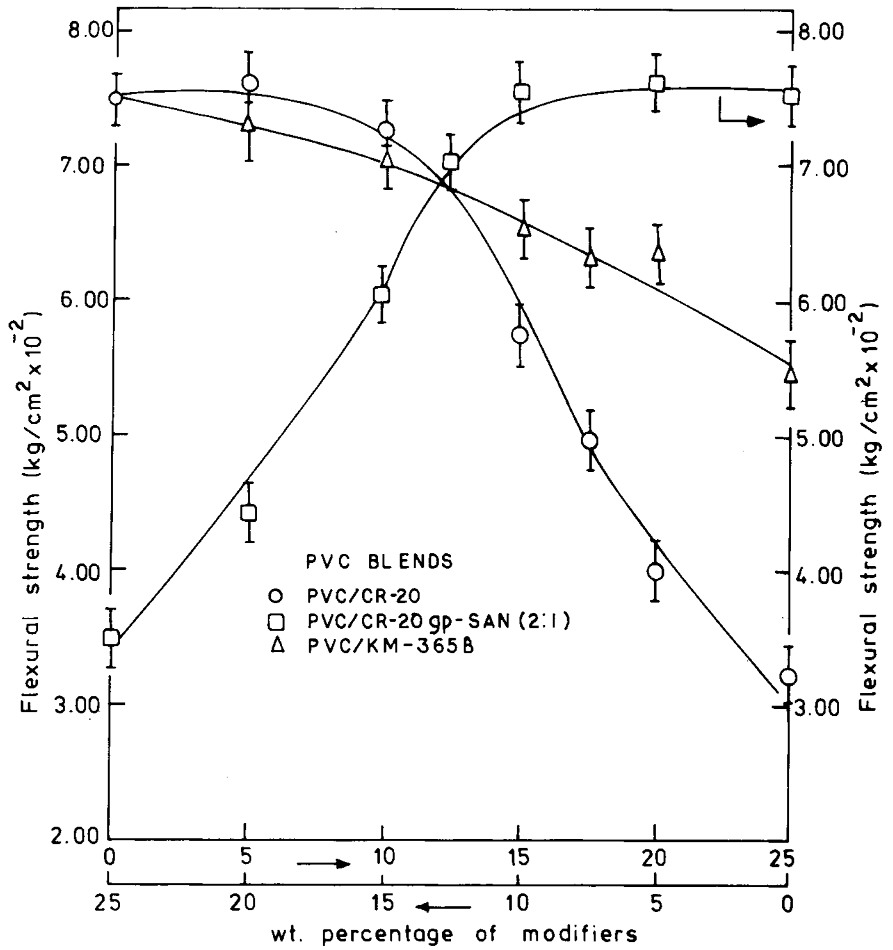


Fig. 7. Flexural strength of PVC blends vs. weight percentage of modifiers: (○) PVC/CR-20; (□) PVC/CR-20-*gp*-SAN (2 : 1); (△) PVC/KM-3658.

in PVC blends:

PVC–KM-365B > CR-20-*gp*-SAN (2 : 1) > PVC–CR-20

3. The performance of various blends with respect to the flexural modulus has been noticed to be similar to that of flexural strength with an exception. The PVC–CR-20 blends show reduction in flexural modulus even at lower concentrations whereas other blends show either marginal increase or no change in flexural modulus prior to the reduction at higher concentrations (> 10%).

Tensile Strength

The tensile properties of PVC blends are tabulated in Tables VI–IX. As expected, the tensile strength and modulus of PVC blends have been found to decrease with the concentration of modifiers. However, the patterns of the reduction in tensile strength were differing in various blends. In brief, the

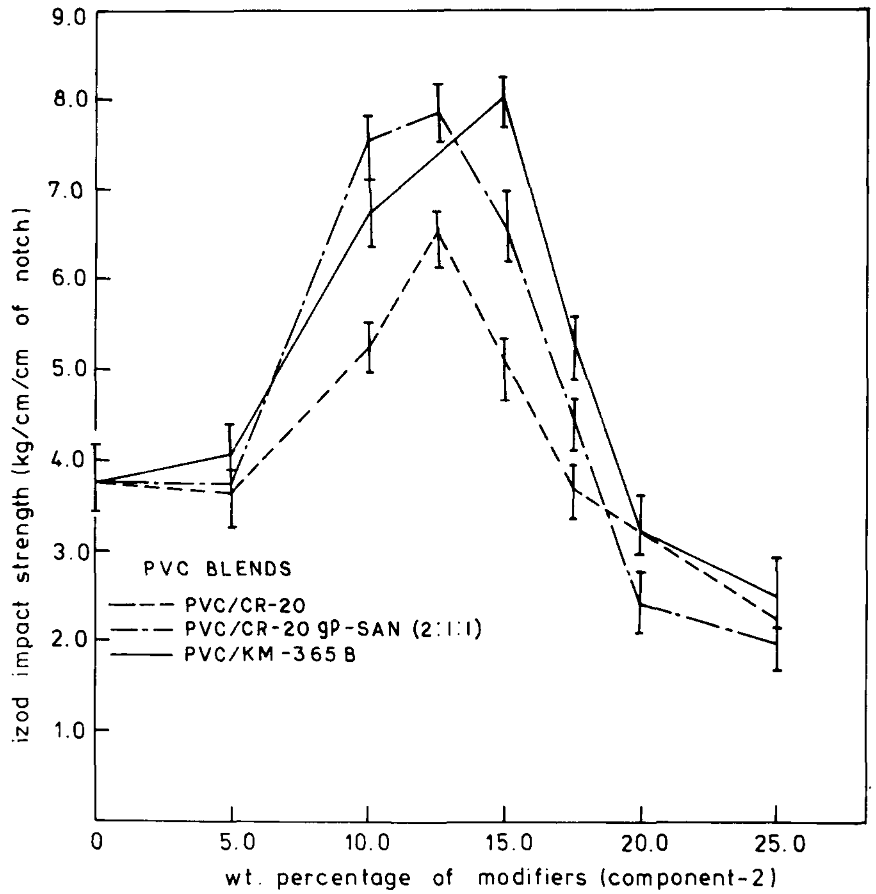


Fig. 8. Izod Impact strength of PVC blends vs. weight percentage of modifiers: (– – –) PVC/CR-20; (– – –) PVC/CR-20-*gp*-SAN (2 : 1 : 1); (—) PVC/KM-3658.

following conclusions may be drawn from the analysis of the tensile strength data.

1. The incorporation of various modifiers results in the reduction of tensile strength of blends.
2. The following trend of tensile strength has been observed among all PVC blends (Table IX):

PVC–CR-20-*gp*-SAN (2 : 1) > PVO–CR-20 > PVC–KM-365B

Impact Strength

The effect of several compositional changes of CR-20 and CR-20-*gp*-SAN (2 : 1) on the impact strength of PVC are reported in Tables VI–IX and are further plotted in Figure 8. The following conclusions may be drawn from impact strength data of various PVC blends.

a. Generally, in the chlororubber-20-based modifiers, the concentrations of modifiers required for optimum impact strength improvement were found to be in the range of 10–15%. Exact optimum concentration, at which maximum impact strength is imparted, could not be pointed out because of the compositional gaps in the experimental results.

b. In brief, the following trend of impact strength has been observed:

PVC–KM-365B > PVC–CR-20-SAN (2 : 1) > PVC–CR-20 blends

It has generally been seen that the incorporation of any impact modifier produces a shift of impact strength vs. composition plot to lower temperatures.[32,33] The addition of impact modifier effectively raises the temperature scale of PVC, making it behave as though it were near its glass transition temperature (T_g). Thus, the optimum dispersion and adhesion of the rubber particles with PVC are the basic requirements of impact modification. The word "optimum" signifies sufficient compatibility, i.e., neither total miscibility nor complete incompatibility between the components. Thus, the behavior of the present system has to be viewed with respect to the chemical nature of the dispersed phase, which decides its dispersibility and adhesion with the continuous phase.

The modifiers used in the present studies are the mixtures of CR-20 homopolymer and its graft copolymers. Every modifier is therefore expected to behave differently. The compatibility of these blends has been discussed earlier. However, it is being further discussed in the context of mechanical properties.

Chlororubber-20 makes compatible blends with PVC. The incorporation of graft copolymers of chlororubber-20 in the matrix of the PVC–chlororubber-20 blend may result in the formation of bigger size domains due to the incompatible nature of the grafted segment of chlororubber-20 copolymer. The graft copolymer is anticipated to develop into bigger size domains due to the precipitation of graft copolymers along with CR-20 domains which make the blends heterogeneous. Thus, the incorporation of graft copolymer of chlororubber-20 in the PVC–chlororubber-20 matrix is expected to provide proper dispersion and adhesion.

The agglomeration of CR-20 domains by incorporation of graft copolymers is expected to be facilitated by the stronger interactions between chemically identical backbone of graft copolymer and chlororubber-20 homopolymers. The grafted copolymers are expected to be absorbed onto the surface of chlororubber-20 domains rather than penetrating into it because of the multiple branches of graft copolymers restricting its penetration into the homopolymer domains.[34–36] Thus, the surface adhesion would be preferred. An optimum dispersion and adhesion of graft polyblends of chlororubber-20 in PVC matrix is therefore expected. However, the extent of it would differ in various blends. The following schematic model of the blends of PVC with various modifiers has been given in Figure 9.

It has been observed that the flexural and tensile strengths of PVC are reduced by the incorporation of the above-mentioned modifiers in its matix. However, the modifier concentration range of 5–15% is the most interesting one since, in this region, the impact strength of PVC is improved without any major sacrifice in the tensile and flexural properties. It may therefore be inferred that, in this particular range, the tensile and flexural properties are

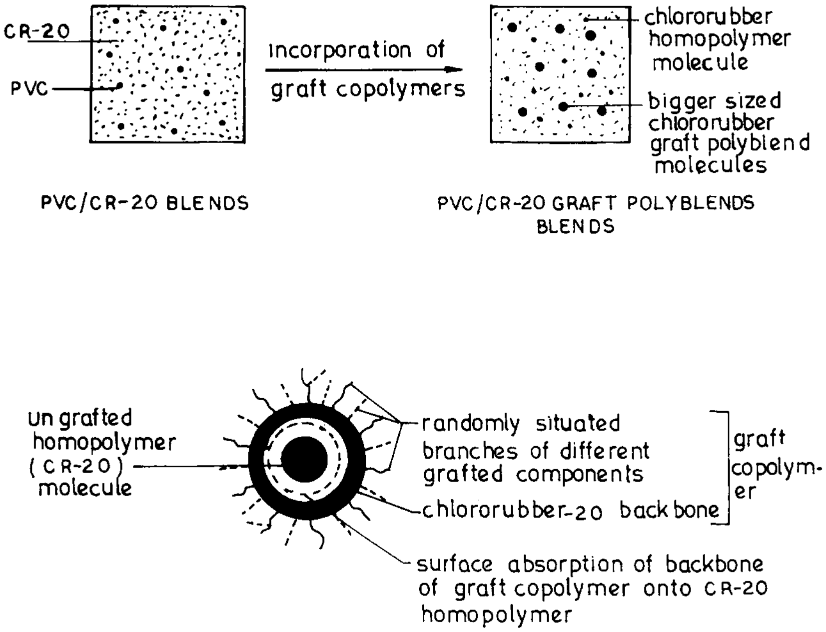


Fig. 9. Schematic diagram illustrating distribution of CR-20 and its graft polyblends in PVC matrix.

mainly controlled by PVC phase, though the modifier phase has a controlling effect on impact strength of the system. The continuous and almost linear variation in flexural modulus of PVC–CR-20 blends with composition is an indication of thorough mixing such that no discrete phase is large enough to exert a controlling effect on the modulus of the blend. However, this behavior has not been exhibited in other systems and in other properties.

Generally, the concept of additive behavior of tensile and flexural properties is used as an indication of the compatibility of the blends, though it is not an unwavering assumption.[37] Various other tests may yield conflicting information. It may be due to the fact that each test may operate on certain molecular mechanism and on certain microscopic levels.[38] Strong polymer–polymer interactions have also been observed in the X-ray diffraction pattern of PVC–CR-20 blends (Fig. 10). The X-ray diffraction peak of PVC is completely distrubed by the incorporation of CR-20 in its matrix. Suresh et al.[10] have observed in PVC–CR-20 blends at higher concentration ($>$ 50%) of CR-20 that the blend becomes completely amorphous and crystallinity of PVC is completely lost. This shows the presence of stronger polymer–polymer interaction, which results in complete mixing of the components. It is quite understandable due to the presence of highly polar chlorine groups in both the constituents.

At higher concentrations of modifiers, the flexural and tensile properties decrease drastically, which may be an indication of the effect of plasticization.[39,40] The flexural moduli and flexural and tensile strengths of various blends such as PVC–KM-365, PVC–CR-20-*gp*-SAN (2 : 1) do not change linearly with composition. This may also be an indication of the presence of

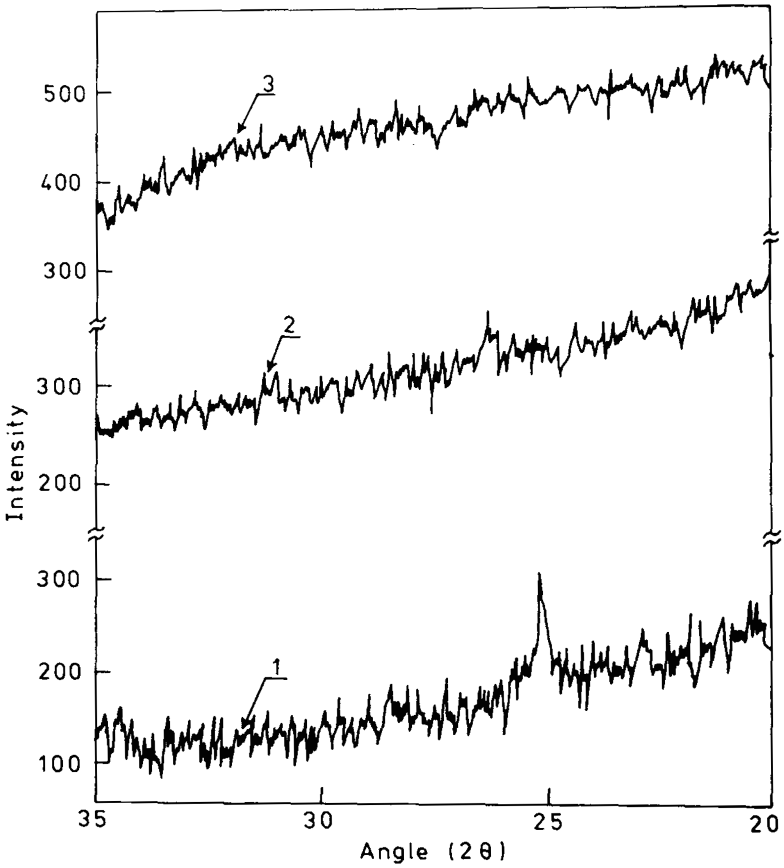


Fig. 10. X-ray diffraction pattern of PVC-CR-20 blends: (1) PVC (100); (2) PVC-CR-20 (90 : 10); (3) PVC-CR-20 (82.5 : 17.5).

such a phase in the matrix which exerts a controlling effect on PVC properties. Thus, there is a possibility of more than two phases in these systems.

The varying behavior of various blends for their flexural and tensile properties as has been stated earlier may be explained on the basis of the relative compatibilities of various modifiers with PVC. It may be one of the main factors in the determination of various physical properties of the blends. It appears that the mixing of the CR-20-*gp*-SAN (2 : 1) modifiers with PVC is more adequate in comparison with CR-20 modifiers because of their better performance as far as tensile and flexural properties are concerned. The word "adequate" mixing refers to the optimum compatibility of the modifers with PVC, which is most suitable for better properties. The adequate mixing in the blends of PVC with various modifiers is provided by the cumulative effect of compatible species chlororubber-20 (in the form of homopolymer and grafted backbone) along with certain incompatible constituents in the form of grafted chains such as PS and PAN. The comparison of various X-ray diffraction patterns of PVC–CR-20 blends with other PVC blends, i.e., PVC–CR-20-*gp*-

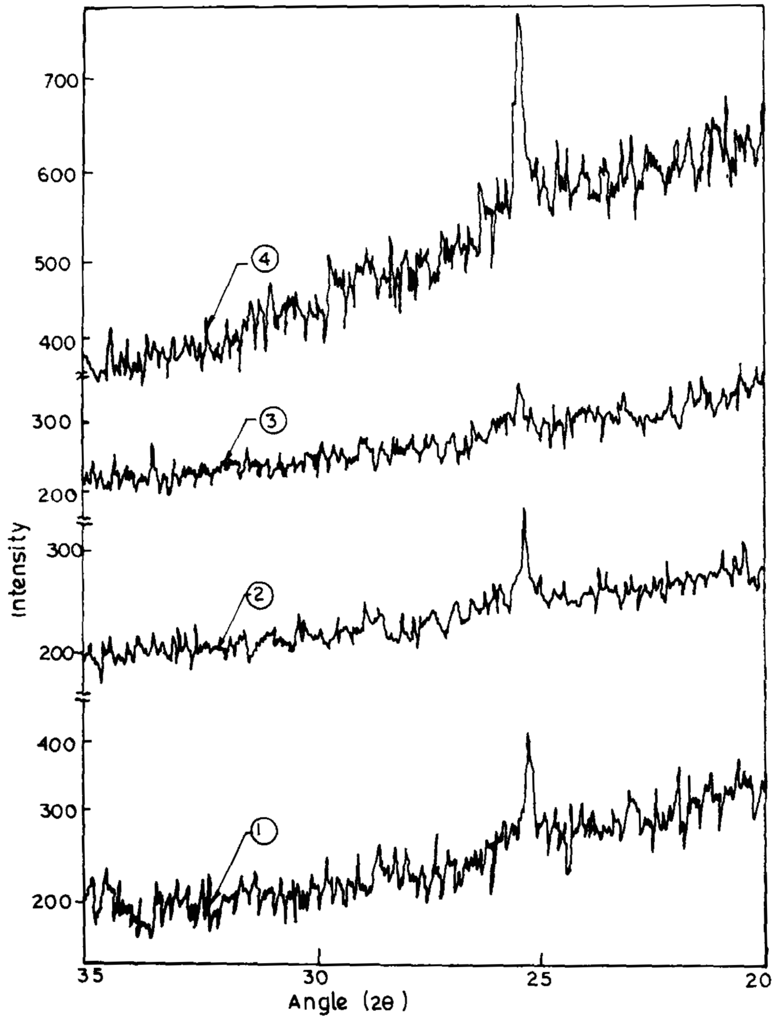


Fig. 11. X-ray diffraction pattern of PVC-CR-20 – *gp*-SAN (2 : 1) blends: (1) PVC (100); (2) PVC–CR-20-*gp*-SAN (2 : 1) (90 : 10); (3) PVC–CR-20-*gp*-SAN (2 : 1) (85 : 15); (4) PVC–CR-20-*gp*-SAN (2 : 1) (80 : 20).

SAN (2 : 1) (Fig. 11) implies that the X-ray diffraction pattern typical of PVC is less disturbed in latter blends (Figs. 10 and 11). This indicates weaker polymer–polymer interaction between the components of these blends. The crystallinity loss, as observed qualitatively from the height of the diffraction peak, is also less in other blends in comparison with PVC–CR-20 blends (Figs. 10 and 11). Thus, the relative compatibility of various components of modifiers makes all the difference in the properties and is the reason behind the varying behavior of these blends.

As observed earlier, the 5–15% concentration range appears to be very interesting since the impact strength of PVC is increased without any major loss in other mechanical properties. The dispersed phase imparts impact

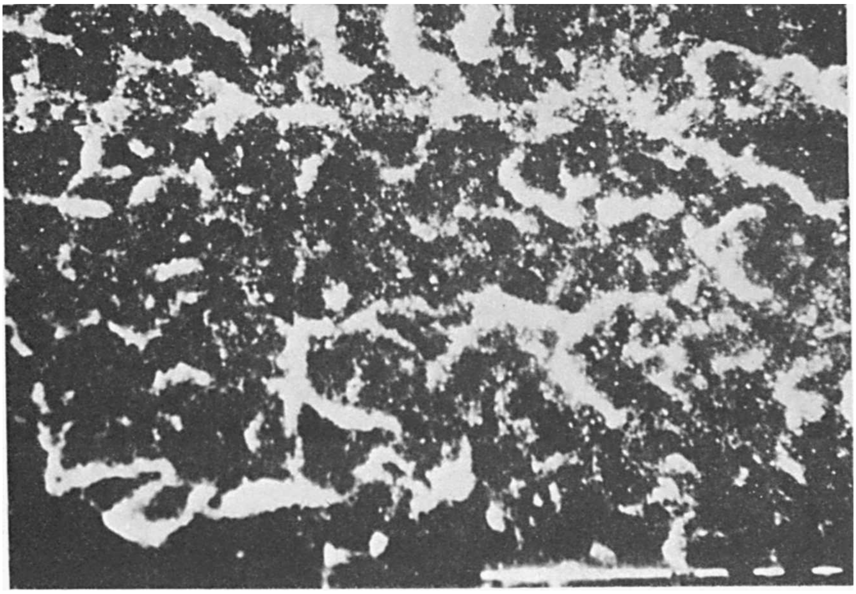


Fig. 12. SEM Photograph of the fractured surface (impact) of unmodified PVC at 260 magnification.

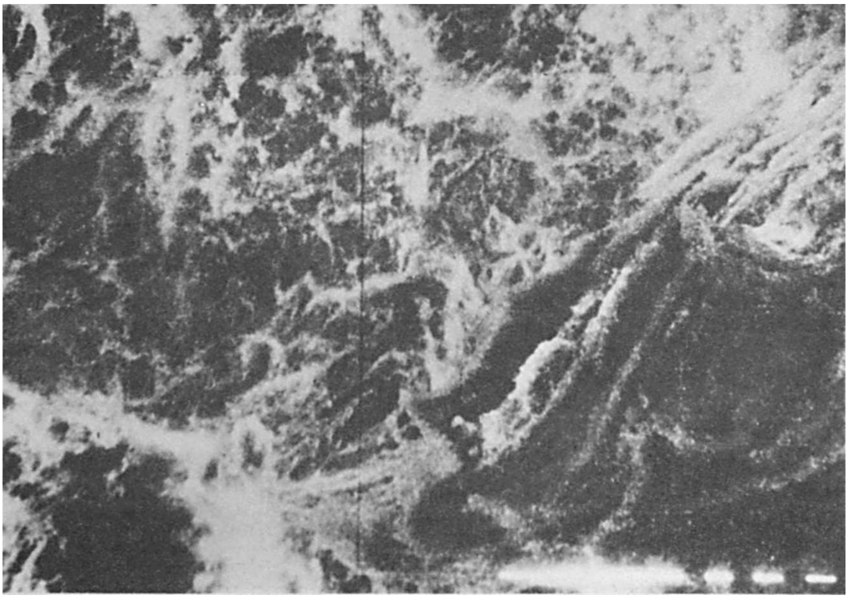


Fig. 13. SEM photograph of the fractured surface (impact) of PVC-CR-20 (90 : 10) blend at 164 magnification.

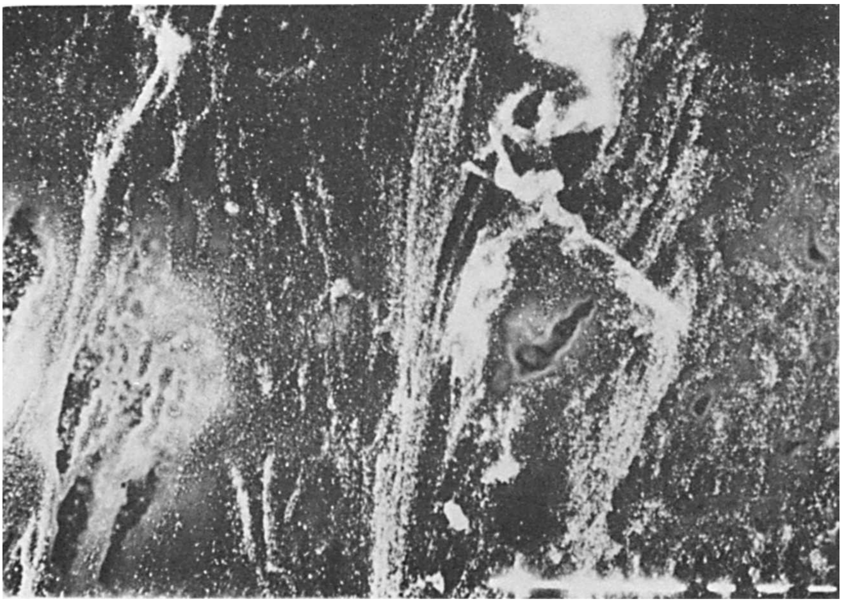


Fig. 14. SEM photograph of the fractured surface (impact) of PVC-CR-20 (85 : 15) blend at 174 magnification.

strength whereas the major PVC phase almost retains its other properties such as tensile and flexural strengths. The impact strength shows the peak and is explicable in terms of various theories on impact modification by elastomeric phase.[32]

The observation of the impact strength patterns of various modifiers implies that the impact strength of blends of PVC with graft polyblends of CR-20 is more than that of PVC–CR-20 blends. Higher strength of these blends in comparison with PVC–CR-20 blends may be attributed to the interlocking of various phases by grafted chains. The triaxial stress generates cavitation either in the adjacent matrix or in rubber particle itself, which results in stretching of the rubber particles.[41,42] The grafting strengthens these rubber particles by interlocking the two continuous phases as in three-dimensional network[42] which may be the reason of higher impact strength in grafted polyblends. However, no craze formation could be detected in the matrix of blends after impact fracture. These concepts require a further detailed study of the relationship of morphology and composition at various temperature to solve the complexity of the problems.

Deformation Behavior of PVC Blends

Various PVC blends have been studied for their impact fracture behavior by scanning electron microscope. Figure 12 shows the scanning electron micrograph of fractured area of unmodified PVC. The brittle nature of the fracture is evidenced by the micrograph. Figures 13 and 14 show the fractured surface of PVC–CR-20 blends at 10 and 15% concentrations of CR-20 components. The ductility as evidenced by stretching of the rubber particles is clearly observed in the SEM micrographs. Thus, the introduction of CR-20 in PVC

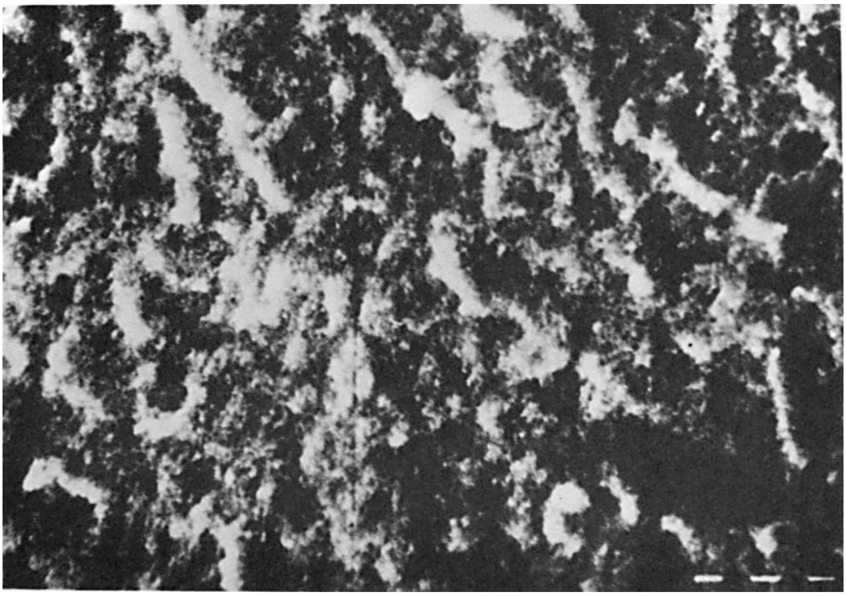


Fig. 15. SEM photograph of the fractured surface (impact) of PVC-CR-20-*gp*-SAN (2 : 1) (90 : 10) blend at 310 magnification.

matrix results in the ductile deformation of the blends. Further, Figure 15 shows the scanning electron micrograph of the fractured surface of PVC–CR-20-*gp*-SAN (2 : 1). The comparison of Figures 12 and 13–15 leads to the conclusion that comparatively less stretching of rubber particles is observed in PVC–CR-20-*gp*-SAN (2 : 1) blends. Thus, the fracture behavior of these blends may be referred to in between the brittle and ductile ones, i.e., may be referred to as semiductile. This change in the fracture behavior of blends from brittle to semiductile is further indicatie of such a phase, which exerts an influence on the properties of these blends.

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