CHAPTER - III

CHAPTER-3

PREPARATION AND CHARACTERIZATION OF BLENDS OF PVC WITH POLY(BUTADIENE)BASED MODIFIERS

PREPARATION AND CHARACTERIZATION OF BLENDS OF PVC WITH POLYBUTADIENE BASED MODIFIERS

3.1. INTRODUCTION

Ideally, two or more polymers may be blended together to form a wide variety of random or structural morphologies, to obtain products that potentially offer desirable combinations of characteristics. However, it may be difficult or impossible in practice to achieve these potential combinations through simple blending because of some inherent and fundamental problems. The method of approach is to select components in such a way that the principal advantages of the first polymer will compensate for deficiencies of the second and vice-versa[1-5]. However, optimization of performance involves a multivariable analysis where the molecular parameters of the ingredients, the interphase and morphology interact. Good Most often, the two polymers with desirable properties are immiscible, which precludes generating a truly homogenous product. This may not be a problem as such because often it is desirable to have two-phase structures[6], which offer definite advantages if mechanical compatibility can be achieved. The modern compatibilization and reactive blending can overcome these problems to some extent but certain unavoidable compromises may have to be made[1-6]. (See Guthrie and Lin, Surface Coatings International (1993); Dyes & Pigments (1992))

Although the term 'compatibility' is often used in a thermodynamic sense to be synonymous with 'miscibility', in technological literature, it is used to describe good adhesion between the components. The term 'miscibility' suggests that the level of molecular mixing is adequate to yield macroscopic properties expected of a single phase material. Components that resist gross phase segregation and/or give desirable blend properties, are frequently said to have a 'degree of compatibility' eventhough in thermodynamic sense they are not miscible[7].

The patented literatuure reveals that the most sought after properties in the blends are toughening (i.e. high impact strength) and processibility, which together account for ~51% of the total. The second group of importance (~25%) includes strength, modulus and the heat deflection temperature.

In this chapter, the preparation of PVC/PBR, PVC/EPBR and PVC/chlorohydrin blends by melt mixing process and the characterization of these blends by various techniques are ~~have been~~ described. An attempt has been made to correlate the nature of the rubbery phase with ~~and~~ the properties of the blends especially the impact strength and the thermal characteristics in order to explore the potentiality of high molecular weight polybutadiene-based rubbery phases as property modifiers to PVC.

poly (Monomer)

3.2 EXPERIMENTAL

This thesis has mixed units cc here and ml elsewhere both are unacceptable (non-SI) Use cm^3

3.2.1. MATERIALS

The following materials were used in the preparations of PVC blends.

a) Poly(Vinyl Chloride)(PVC) : Suspension polymerized, (Indovin) (K-67) supplied by M/s. I.P.C.L Baroda.

Properties of PVC.

Inherent viscosity (I.V.) : 0.92 Units?
Apparent Bulk Density : 0.50 g ~~/cc~~ cm^3
Particle size distribution : 5 max.(%retension on 50 mesh) ? distribution
Porosity : 0.26 - 0.36 cc/g cm^3

b) Poly(butadiene) rubber (cis- 1,4) (PBR) : This was supplied by M/s. I.P.C.L. Baroda.

Properties of PBR.

How determined

Intrinsic viscosity in toluene : 2.48 dl/g
Number Average Molecular weight ($\bar{M}n$) : 2.3 x 10^5 Daltons or g mol^{-1}
Weight Avarage Molecular weight ($\bar{M}w$) : 5.9 x 10^5 "
Poly dispersity ($\bar{M}w/\bar{M}n$) : 2.52

Units needed

c) Epoxidized Poly(butadiene), (EPBR) : This was synthesised in the

Characterisation eg $\bar{M}n$, $\bar{M}w$, $\bar{M}w/\bar{M}n$ for EPBR?

Characterise?

laboratory. The details of EPBR used are given in Chapter II.

d) Chlorohydrin derivative of PBR : This was also synthtsised in the laboratory. The details ofChlorohydrin used are given in chapter - II.

e) di-n-Octyl Tin Mercaptides (TM 181), M/s. A.L.AChemicals, Bombay.

f) Calcium stearate - National Chemicals,Baroda.

g) Processing aid - Acrylic type (Acryloid K-175; Rohm & Haas, U.S.A.)

h) Stearic acid - National Chemicals,Baroda.

Proper addresses more useful.

3.2.2. PROCESSING

3.2.2.1. Compounding of rigid PVC.

Prior to blending PVC with modifiers, the powdered PVC resin was initially dry blended with additives in a Brabender Plasticorder (model - PLV 151) using a cam -type mixer with a rotor speed of 60 rpm at 88°C, for 10 min.

Dry blending of PVC in accordance with a ~~S~~standard compounding recipe[8] was ~~done.~~ undertaken.

3.2.2.2. Melt mixing.

The melt mixing of PVC resin with various modifiers (0-15 wt%) ~~were~~ was performed at 170 °C maintaining the rotor speed at 50 r.p.m in the Brabender Plasticorder. Formulations for various binary blends are given in Tables 3.1 to 3.3.

Table 3.1

Formulations for PVC/PBR blends.

Sr.No.	Blend constituents	Blend code	PVC wt %	PBR wt %
1	PVC	P	100.0	-
2	PVC/PBR	a_1	97.5	2.5
3	PVC/PBR	a_2	95.0	5.0
4	PVC/PBR	a_3	90.0	10.0
5	PVC/PBR	a_4	85.0	15.0

Table 3.2

Formulations for PVC/EPBR blends

Sr. No.	Blend constituents	Blend code	PVC wt%	EPBR wt%	EPBR degree of epoxidation (mol %)
1.	PVC/EPBR	b_1	90.0	10.0	5
2.	PVC/EPBR	b_2	90.0	10.0	10
3.	PVC/EPBR	b_3	90.0	10.0	15
4.	PVC/EPBR	b_4	90.0	10.0	20
5.	PVC/EPBR	b_5	90.0	10.0	25
6.	PVC/EPBR	c_1	97.5	2.5	25
7.	PVC/EPBR	c_2	95.0	5.0	25
8.	PVC/EPBR	c_3	90.0	10.0	25
9.	PVC/EPBR	c_4	85.0	15.0	25

Table 3.3

Formulations for PVC/Chlorohydrin blends

Sr. No.	Blend constituents	Blend code	PVC wt%	PBR Chlorohydrin wt%
1.	PVC/ PBR chlorohydrin	d_1	97.5	2.5
2.	PVC/ PBR chlorohydrin	d_2	95.0	5.0
3.	PVC/ PBR chlorohydrin	d_3	90.0	10.0
4.	PVC/ PBR chlorohydrin	d_4	85.0	15.0

How determined ? —
Extent of Cl uptake
— heterogeneous product ?

Torque developed during melt mixing were recorded. Prior to melt mixing each blend composition was mixed thoroughly in an ordinary mixer. Then melt mixing was carried out in the mixing chambers maintained at 170°C and at 50 rpm. The total mixing time of PVC with modifier was fixed at 8 minutes in all the cases. For recording the Plastograms, a Brabender Plastograph was used under the following conditions for each composition.

Volume of mixing chamber : 60 ~~cc.~~ cm^3
Chamber temperature : 170°C.
Torque recording range : 0-100 Nm.

The molten mix was then quickly removed from the chamber and cut into small pieces and again extruded at 150 - 170 °C for obtaining pellets. The extruded material was obtained in the form of cylindrical strands, and the strands were cut into regular small cylindrical pellets of 3 mm length by a pelletizer.

The pellets were compression molded in between two polished stainless steel cases (1 mm thickness). Small pellets were stacked appropriately and molded at 180 ± 2°C as shown in Table 3.4. The whole system containing blend pellets were inserted in between the preheated upper and lower platen of hydraulic press having temperature control system. After insertion of the material the upper and lower platen of the press were brought close to each other for 2 minutes. Then the material was compressed at a pressure of 10 ~~K~~kg/cm^2 for one min, 60 ~~K~~kg/cm^2 for 1/2 min and finally the stacks were molded by applying 100 ~~K~~kg/cm^2 for 1 min. This was followed by immediate cooling of the system with cold water.

The summary of the operation of the compression molding of PVC and its blends ~~are~~ is given in Table 3.4. The specimens for various testings were cut and machined from the prepared sheets. Prior to testing the specimens were annealed at 60°C for 48 h.

Lower case k for kilo

Table 3.4

Compression Molding operations of PVC Blends

Sr. No.	operations	Temp °C	Pressure Kg/cm^2	Time min.
1.	Contacting of upper and lower platen of hydraulic press.	180	Atmospheric	2
2(a).	Contact under pressure	180	10	1
2(b).	Contact under pressure	180	60	1/2
3.	Molding operations	180	100	1

3.2.3. CHARACTERISATION OF THE BLENDS

3.2.3.1. Density

The density measurements of PVC and its blends were carried out ~~by~~ using the specific gravity method, according to ASTM D792. The values of the densities of PVC and its blends were compared with theoritical densities obtained from ' the rule of mixtures.'

Which is? (ref)?

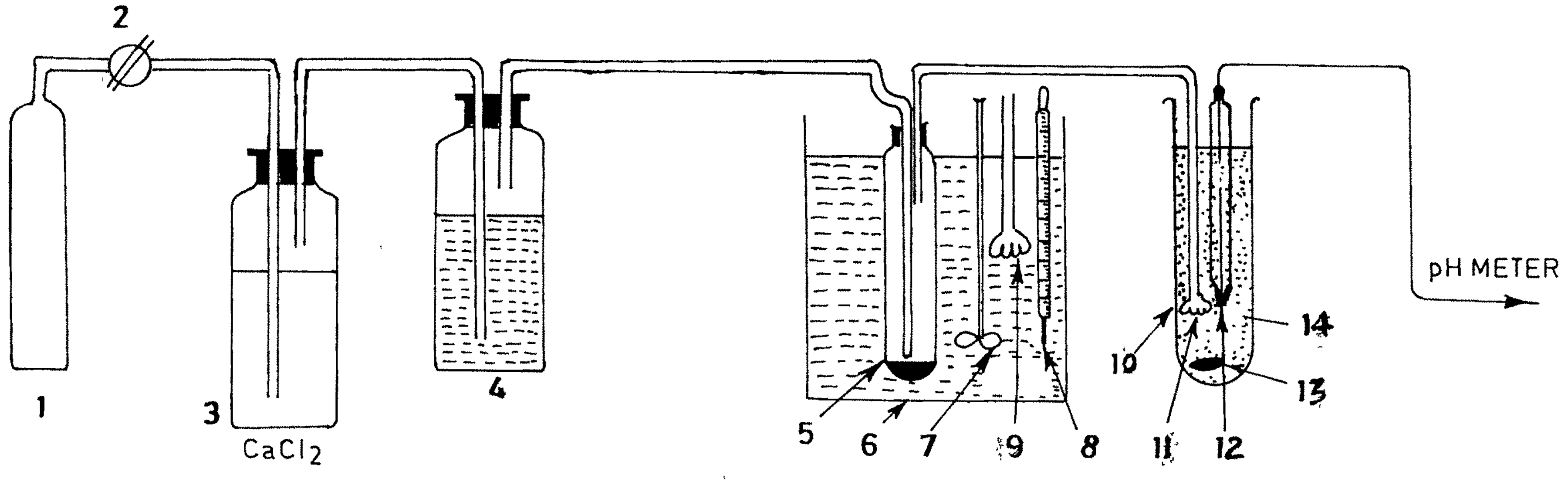
3.2.3.2. Torque measurements :

Torque developed during the mixing of PVC and its binary blends with various modifiers was measured ~~by~~ using a Brabender torque-rheometer coupled with internal mixing head. The variation of torque with time was recorded. The mixing temparature, rotor speed and mixing time of the polymer inside the mixing chamber were kept at 170 ± 1 °C, 50 r.p.m. and 8 min respectively.

3.2.3.3. Thermal studies of PVC and its blends.

Thermo-Gravimetric Analysis (TGA) : Thermogravimetric studies of PVC and its blends were carried out on a Shimadzu, Thermal Analyser DT - 30 at a heating rate of 10°C/min in a N_2 atmosphere from 30°C to 700°C. Samples of ~5mg in the form of powder ~~was~~ were used for analysis.

HCl evolution technique : In this technique, thermal stability is measured on the basis of the amount of HCl gas evolved during degradation. The evolved HCl was measured by pH meter (Systronics 335). The ~~E~~experimental set up used for these studies has mainly two parts. The first part consists of the sample holder, a narrow three necked flask, kept in oil bath maintained at 90 ± 1°C. The second part consists of an absorbtion vessel



1. N_2 CYLINDER
2 CONTROL VALVE
3 $CaCl_2$ TRAP
4 CONC H_2SO_4 TRAP
5 SAMPLETUBE
6 THERMOSTAT (REGULATED AT 190 ± 1°C)
7. STIRRER
8 THERMOMETER
9 HEATING ELEMENT ATTACHED WITH TEMP CONTROLLING UNIT
10 RECEIVING VESSEL
11 CINTERED GAS PASSING TUBE
12. ELECTRODE (FOR pH METER)
13 MAGNETIC STIRRER
14 DISSOLVING MEDIUM

FIG 3 12 EXPERIMENTAL SET UP FOR THERMAL STABILITY MEASUREMENTS OF PVC BLENDS BY HCl EVOLUTION TECHNIQUE containing 100 ~~ml~~ cm^{3} of 2.02 x 10^{-3} ~~N~~ M NaOH solution. Figure 3.12 shows details of the experimental set up. The thermal stability measurements were carried out by continuously monitoring the pH of the solution in which the decomposition product (HCl) of the PVC blends was being dissolved. 500 mg. of polymer ~~was~~ were heated in the narrow flask at 190 ± 1°C. The evolved gas was collected by a continuous flow of dry preheated N_2 bubbled through sintered glass into 100 c.c. cm^{3} of 2.02 x 10^{-3} ~~N~~ M NaOH solution. The solution was constantly stirred at about 30°C, and the change of pH was monitored using a digital pH meter.

The induction period for HCl evolution was taken as the measure of the stability of PVC or its blends. A blank experiment was carried out initially. The sample weight was kept constant in all the cases.

3.2.4 MICROSTRUCTURAL STUDY

3.2.4.1 Microscopy

The fracture surfaces of the specimens were studied using a Scanning Electron Microscope (SEM) JEOL-JSM 35C. using 15 KV kV operating voltage. The impact fractured samples were mounted on brass stubs using

[illegible]

an adhesive. All the samples were coated with gold in a JEOL JFC 1100 10n sputtering unit. This gives a conductive layer for electron & heat dissipation.

3.2.4.2 Infrared spectroscopy:

Infrared spectroscopic studies of processed PVC and some of its blends were carried out using a ~~by~~ Fourier Transform Infrared Spectrometer (F.T.I.R.) Model IFS 113V. Films of the samples with uniform thickness were used for analysis.

3.2.4.3 X-Ray Diffraction :

X-Ray Diffraction Analysis was carried out by monitoring X-ray diffraction patterns between 5° - 25° Bragg angles at the scanning rate of 2° per minute by X-ray diffractometer (Philips PW 1140) using Ni -filtered Cu K_α radiation.

3.2.5 PERFORMANCE PROPERTIES

The specimens were tested in a laboratory environment temperature at 24 ± 1°C to determine the following mechanical properties:—

3.2.5.1. Tensile properties :

Tensile properties of different blends were ~~carried~~ assessed ~~out by~~ using compression molded specimens according to the ASTM D 638 test method on an Universal Testing Machine (Instron 1195) at 25°C. The load displacement curve was recorded. Testing was carried out under the following conditions :

Cross head speed - 5 mm/min.
Chart speed - 10 : 1
Full scale loading - 500 ~~Kg~~. kg
Gauge separation - 9.6 cm~~s~~.

The ~~T~~tensile strength and ~~T~~tensile modulus of the blends were determined as follows :

Tensile Strain = Chart Displacement / (Gauge Separation) (chart speed)

Tensile Stress = (Load) / (original cross sectional area of test specimens)

Tensile Strength = Max. Load (at yield or break) / (Original cross sectional area of test specimen)

$$= W\,(kg/cm^2) / T \times d \quad \text{———————} \quad 3.1$$

where W, is the maximum load,
T, is the thickness of the sample
and d, width of the sample in the fractured region.

Tensile modulus = Tensile stress/Tensile strain

3.2.5.2 Flexural properties

The flexural strength of PVC and its blends was measured ~~by~~ using a Universal Testing ~~Machine~~ unit, according to ASTM D-790. Testing was carried out under the following conditions :

Cross head speed : 1.3 m.m/min. mm/min
Jaw separation : 5.1 cm.
Chart speed : 20:1
Full Scale load : 50 k g. kg

The specimens were conditioned according to ASTM standards prior to their testing. Testing conditions were kept constant for all the blend samples. The following equations have been used to calculate flexural strength and modulus. ×

Flexural strength = 2wl (kg/cm^2) / 2bd^2 ———————3.2

Where ~~w~~ W - load at fracture
l - span length
b - width of the sample
d - thickness of the sample.

The flexural modulus was calculated as the ratio of stress and strain for Hookean behavior. ?

Flexural modulus = wl^3 (kg/cm^2) / 4 bd^3 C —————3.3

l^3 = volume cm^2 = area ?

where, w is the value of load in kg and 'c' is the deflection corresponding to the load.

3.2.5.3 Impact strength :

Neat PVC and its blend samples were tested for their impact strength using the Avery Izod impact testing machine 43 -1 (TMI) in accordance with ASTM D256-5 method.

The specimens were machined from originally prepared sheets, to ~~obtain~~ provide the dimensions of an impact specimen. The notch was carefully milled into the specimens to concentrate the stress and direct the fracture. Notched specimens were clamped in a vi~~se~~ce with the notch facing the direction of the impact.

A pendulum was raised to a fixed height, and then released to break the sample. At least 5 samples for each blend were tested with the pendulum of 75 kg load.

3.2.5.4 Dynamic Mechanical Analysis.

Dynamic mechanical analysis was carried out on a Rheomotrics Dynamic Spectrometer (RDS-7700). Samples prepared were of approximately 0.3 cm/thickness and 2.5 cm/diameter. The samples were kept in between ~~Cone & plate~~ cone & plate and Parallel plate. Direct readings of Tan δ and G” were noted as a function of temperature. Measurements were made at 5 °C/ min intervals keeping the frequency at 6.3 rad/sec. The maxima in the loss tangent vs temp~~a~~erature curves were taken as the glass transition temperature (Tg).

7

3.2.5.5 Heat Deflection Temperature (HDT) :

The ~~H~~heat ~~D~~deflection ~~T~~temperature of PVC blends (under flexural load) was determined in accordance with ASTM D 648 -82.

The test specimen was tested as a beam with the load applied at its centre which was immersed in a heat transfer medium (Silicon oil) and was well stirred during the test so as to provide a means of raising the temperature at the rate of 2°C /min. The metal supports for the load ~~was~~ were ~~applied~~ placed on the top of the specimens vertically and midway between the supports. The temperature of the medium was measured when the test bar deflected 0.25 mm which is the deflection temperature under flexural load of the test specimen. Depending upon the geometry of the specimen, the load required was calculated as follows :

$$p = (2.s.b.d^2) / (3.L)$$

In this formula,

p = load,

s = maximum stress in the specimen

b = width of specimen

d = depth of specimen

L = Length of span between supports.

Before starting a new test, the temperature of the heating bath was maintained at about 25°C. During the test, five minutes after applying the load, the scale of the dial gauge was pointed to zero and then heating was started. Three specimens of every blend prepared were tested and the average value was taken as HDT of the blend. Mean or spread.

V.I.P since the differences in values are small

3.2.5.6 Rockwell Hardness:

Rockwell Hardness testing of PVC and of all its blends was carried out according to ASTM D 785. by using Rockwell Hardness Tester-ACCO Wilson Instrument Division. For the hardness measurement the 'R' Rockwell hardness scale was used.

3.3 RESULTS AND DISCUSSION

The compatibility of the components in a polymer blend is important, since it decides the microdomain structure of the blends, which in turn decides the properties, especially the mechanical properties. PBR, EPBR and the chlorohydrin derivative of PBR differ in their chemical nature and hence the blends of PVC with these rubbery phases are expected to behave quite differently. (depends on environment)

Blends of PVC with PBR, EPBR and chlorohydrin derivative of PBR of varying composition were prepared by melt mixing and these blends were characterized by the following techniques. (conditions of melt mixing)

3.3.1 DENSITY

Experimentally determined densities of neat PVC, the modifiers and the blends are given in Table 3.5. All the blends show densities lower than that of neat PVC and with the increasing modifier concentration, the densities are found to decrease. Table 3.5 also gives the theoretical densities of the blends calculated by using the expression

$$\frac{1}{\delta} = \frac{W_1}{\delta_1} + \frac{W_2}{\delta_2}$$

where, δ is the density of the blend, δ_1 and δ_2 are the densities of the pure components and W_1 and W_2 are the weight fractions of the respective parent polymers.

Table 3.5

Densities of PVC and its blends.

Blend code	Theoretical (calculated)	Experimental	Blend code	Theoretical (calculated)	Experimental
P	1.380	1.380	c_1	1.365	1.364
a_1	1.363	1.361	c_2	1.350	1.356
a_2	1.346	1.344	c_3	1.322	1.332
a_3	1.314	1.316	c_4	1.295	1.298
a_4	1.284	1.281	d_1	1.368	1.366
b_1	1.316	1.314	d_2	1.356	1.364
b_2	1.317	1.316	d_3	1.334	1.344
b_3	1.319	1.324	d_4	1.313	1.320
b_4	1.320	1.330			
b_5	1.322	1.332			

Densities of modifiers:

$R = 0.920$

$E_1 = 0.931$

$E_2 = 0.936$

$E_3 = 0.945$

$E_4 = 0.952$

$E_5 = 0.960$

$E_6 = 1.028$

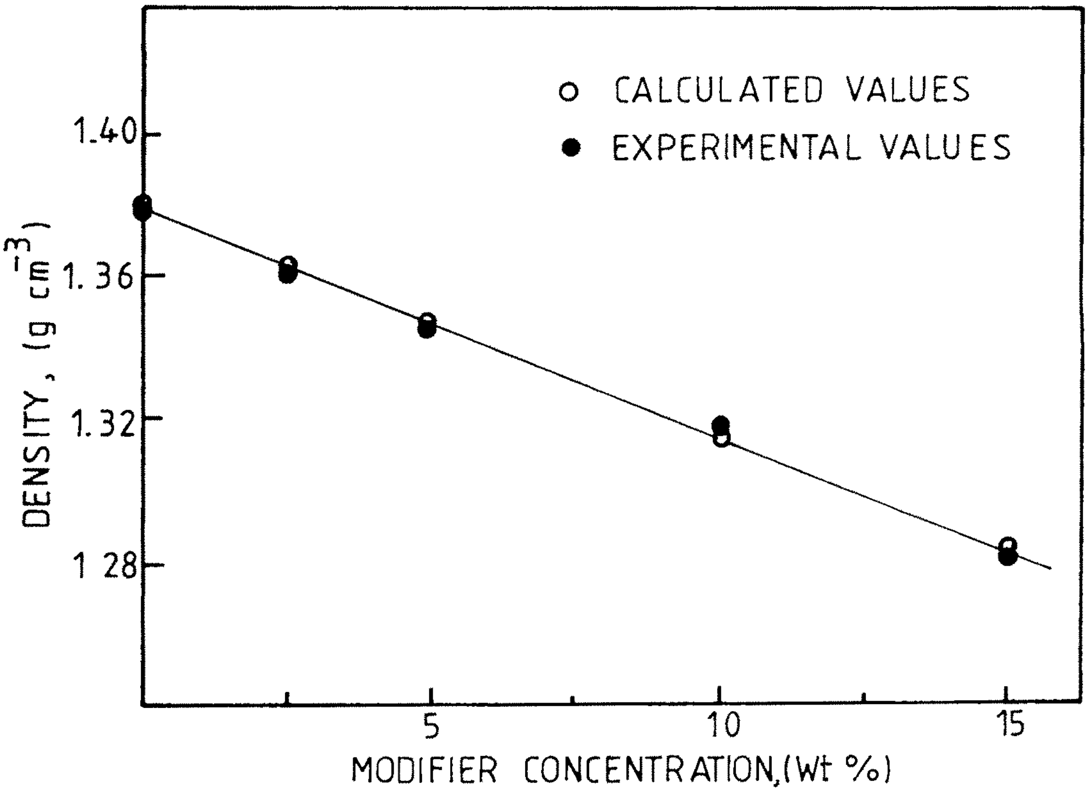


FIG. 3.1 DENSITY CHANGES OF PVC/PBR BLENDS

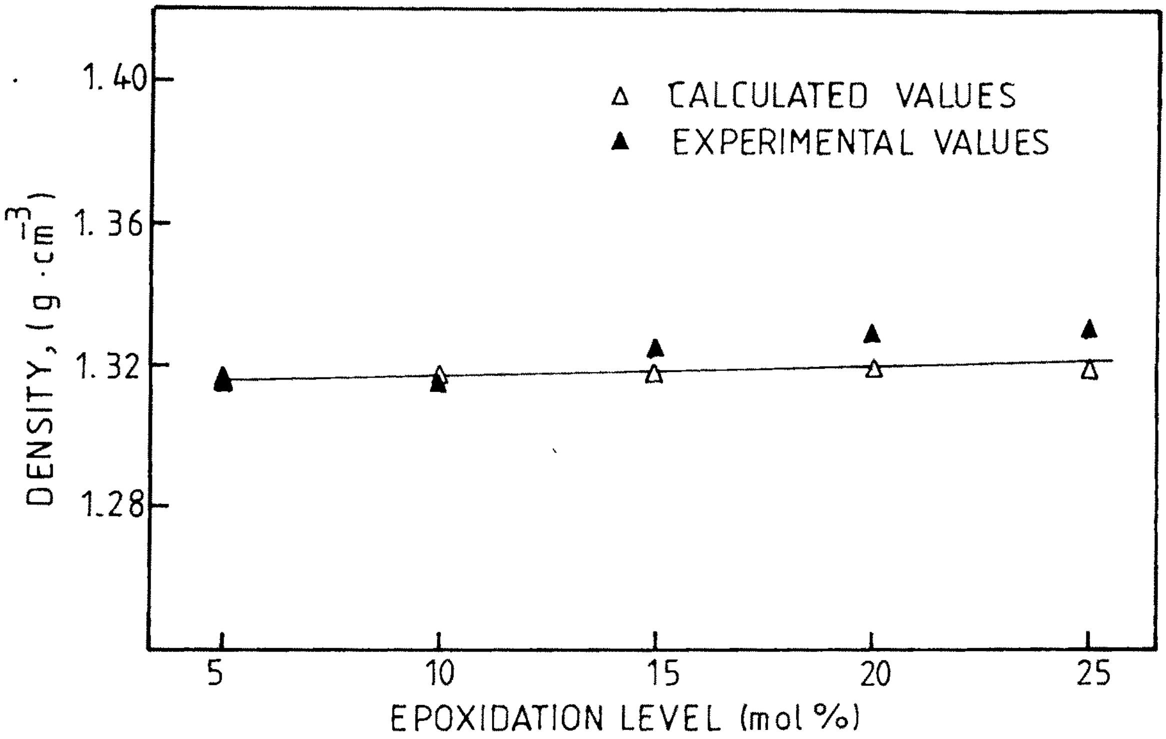


FIG 3 2 DENSITY CHANGES OF PVC/EPBR, (b_1 - b_5) BLENDS

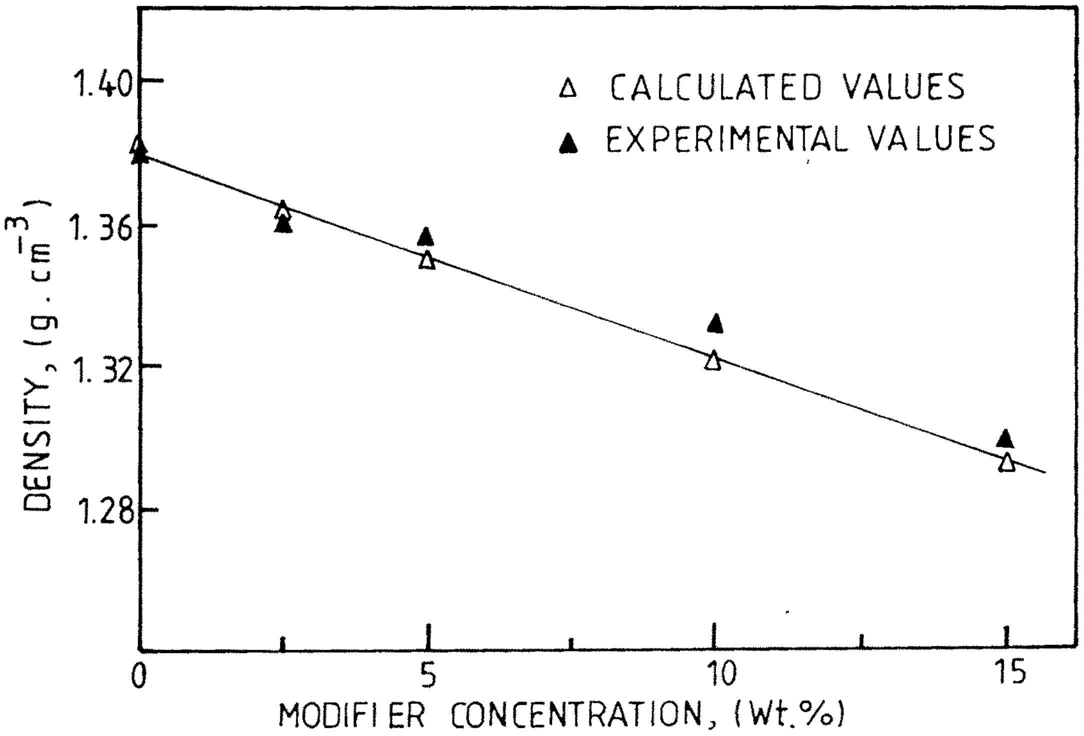


FIG 3.3 DENSITY CHANGES OF PVC/EPBR, (C_1 - C_4) BLENDS

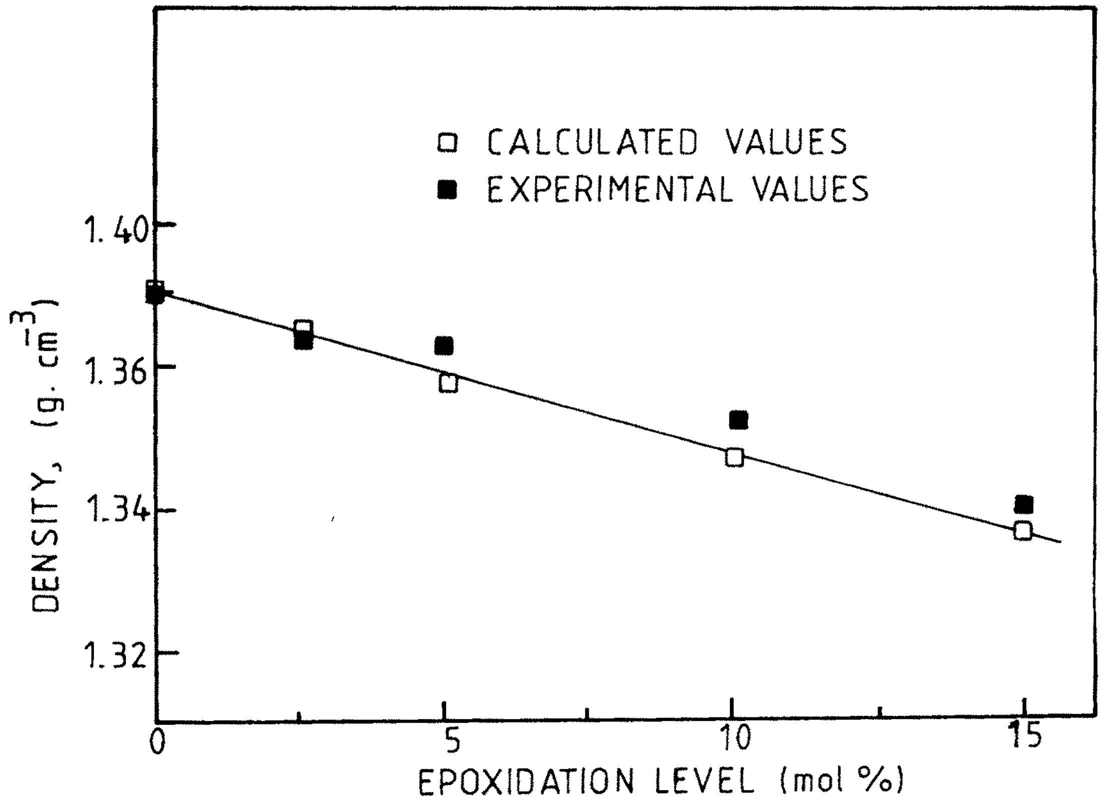


FIG.3 4 DENSITY CHANGES OF PVC/CHLOROHYDRIN, (d1 - d4) BLENDS.

Spread
w. respect
to the
three values
in each
test.

The experimental densities for PVC/PBR blends (a_1, a_2, a_3 and a_4) are very close to the theoretical values and appear to be linear additive (Fig. 3.1). ? This may be due to the fact that the non polar PBR is incompatible with polar PVC. Epoxidation of PBR introduces polarity onto the backbone which may induce a certain degree of compatibility with PVC[9,10]. This is reflected in slightly higher experimental densities than the corresponding theoretical densities in the case of PVC/EPBR blends (b_1 to b_5) especially at higher epoxidation level (Fig. 3.2). Similarly, PVC/EPBR blends (c_1 to c_4) (Fig. 3.3) as well as PVC/Chlorohydrin (d_1 to d_4) blends (Fig. 3.4) show increase in their experimental densities especially at higher wt% of modifiers in blends. This is in accordance with the observation that a strong intercomponent interaction leads to a measurable negative volume of mixing[11,12]. However, to make more accurate comparison for the actual state in which the blend exists the calculated specific volume for the blend must employ pure-component volumes for the same state[7].

3.3.2 TORQUE MEASUREMENTS

Blending with PVC, especially of high molecular weight modifiers is difficult. Commercial PVC is a high viscosity resin at suitable processing temperatures 160-200°C. No At 200°C and above decomposition occurs rapidly, hence melt temperatures of say 210°C can be tolerated for only about 1 min. Therefore, adequate and suitable blending conditions become important to ensure proper mixing at the same time avoiding undesirable degradation reactions. Moreover, properties of the blends are governed by blending conditions[13,14].

Blends of PVC with various modifiers were prepared on Brabender Plasticorder by optimising the feed, rotor speed and temperature. Feed was maintained at ~80% of the mixing chamber volume and the rotor speed was kept constant at 50 r.p.m. Preliminary experiments under these conditions showed that initial mixing temperature of ~170°C was adequate. Heat generated with the progress of mixing lead to an increase in temperature to about 195-200°C. With the initial temperature above 170°C degradation was observed beyond 8-9 minutes of mixing as recognised by the light yellow colour developed by the blends. Therefore, in all the cases the mixing was carried out till 8 minutes at 170°C.

The mixing torque-time curves of blends of PVC with different modifiers and at various compositions are shown in (Fig. 3.5-3.8).

In all the cases, addition of rubbery phase decreases the maximum mixing torque as compared to neat PVC and the maximum is attained in about 5 min, showing that under similar conditions, the time to melt and fuse the PVC particles is almost constant. Homogeneous blends are formed after about 6 minutes of blending. Prolonged mixing beyond 8 min results in degradation of both the components as seen from the drops in mixing torques.

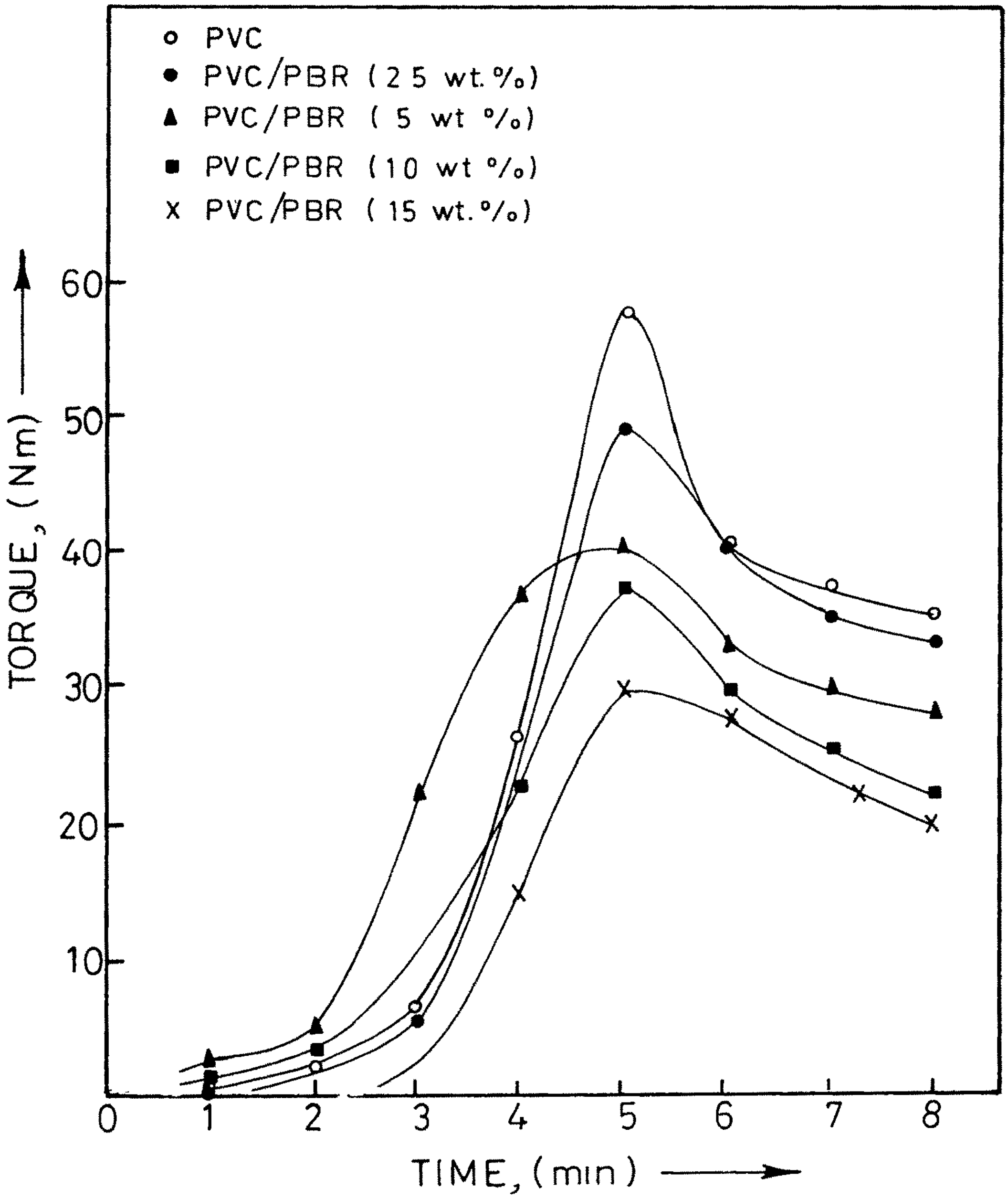


FIG.3 5 MIXING TORQUE–TIME CURVES OF PVC AND ITS BLENDS WITH PBR IN DIFFERENT CONCENTRATIONS

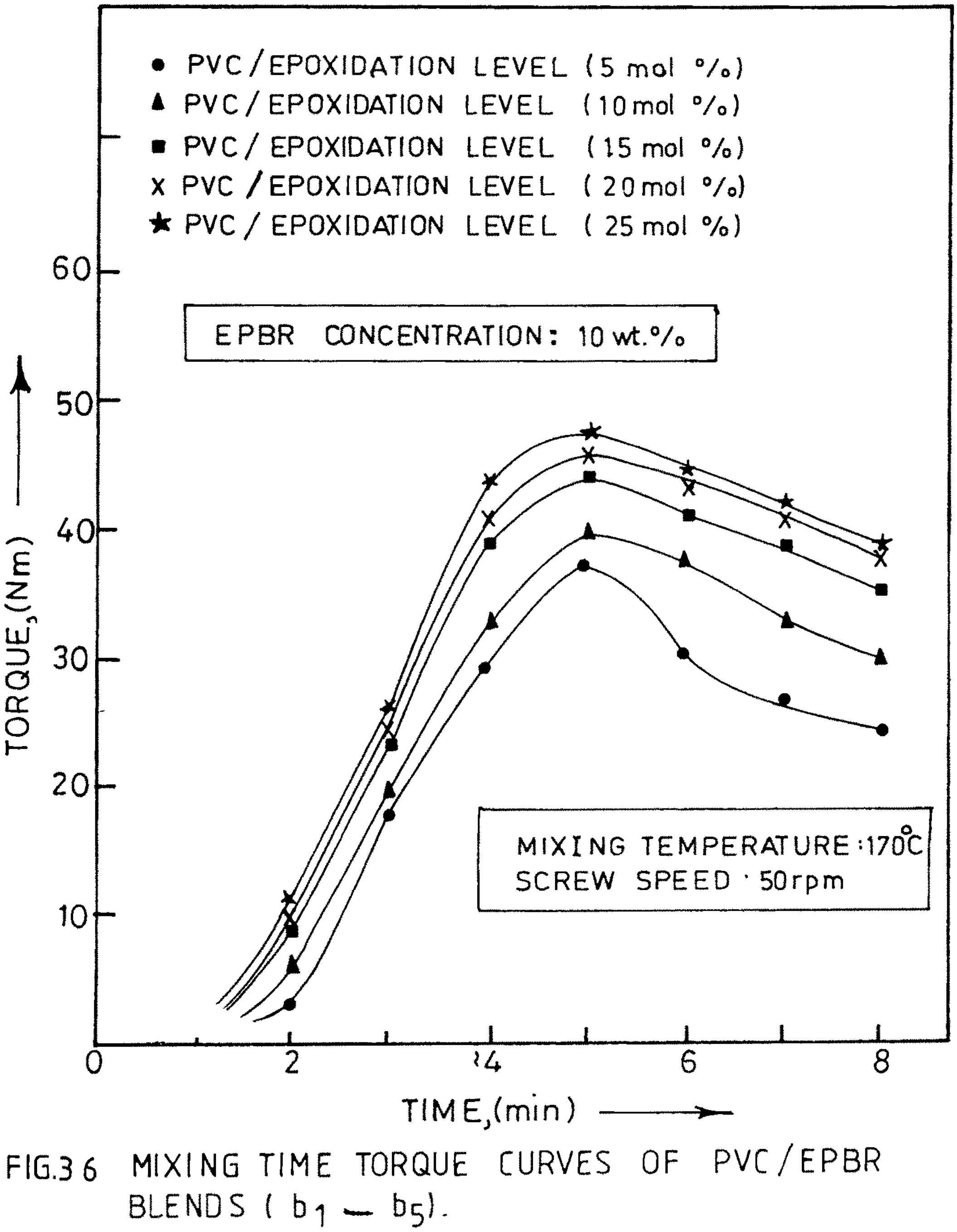


FIG.3 6 MIXING TIME TORQUE CURVES OF PVC/EPBR BLENDS (b_1 – b_5).

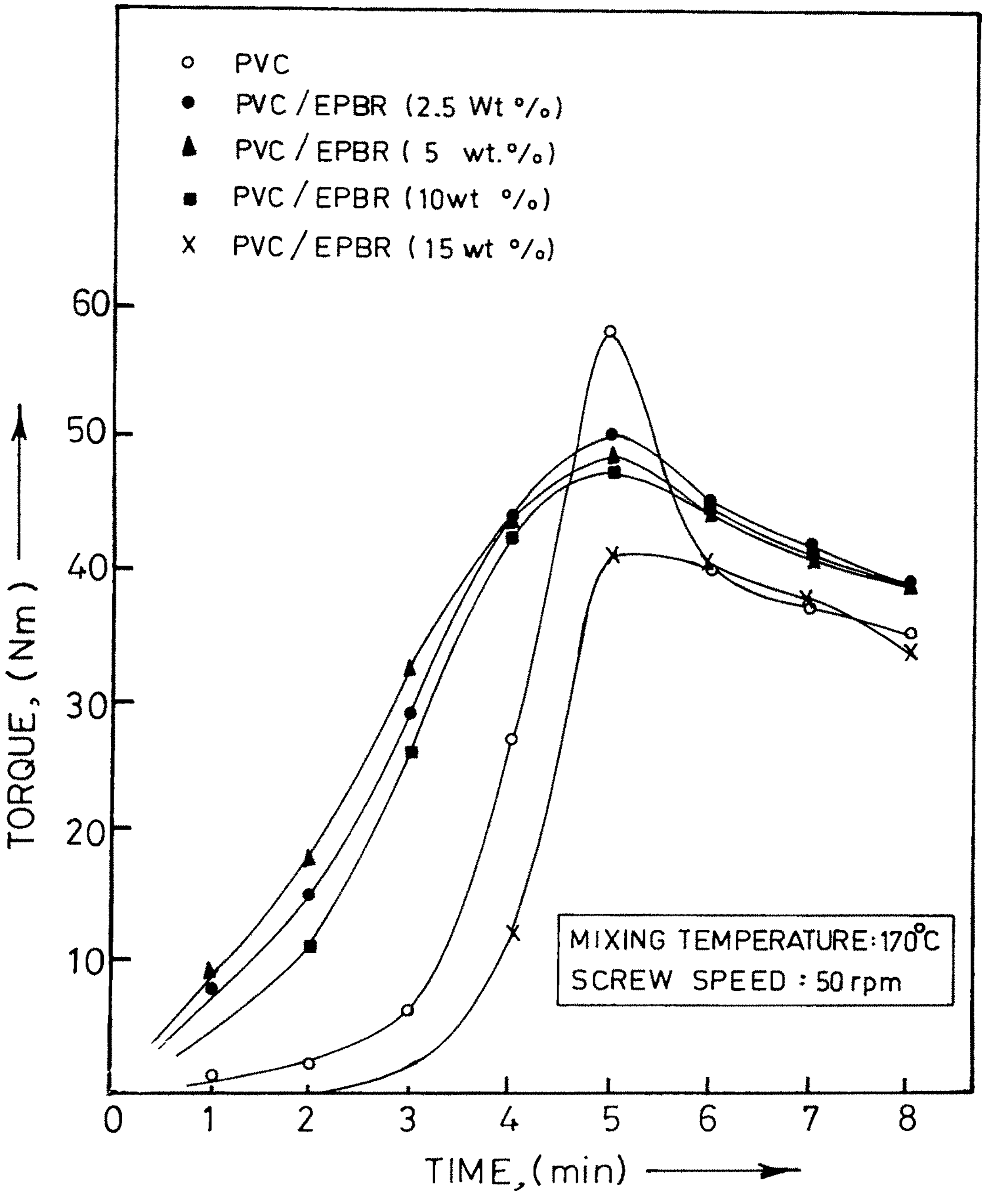


FIG. 3.7. MIXING-TORQUE TIME CURVES OF PVC AND ITS BLENDS WITH EPBR IN DIFFERENT CONCENTRATIONS

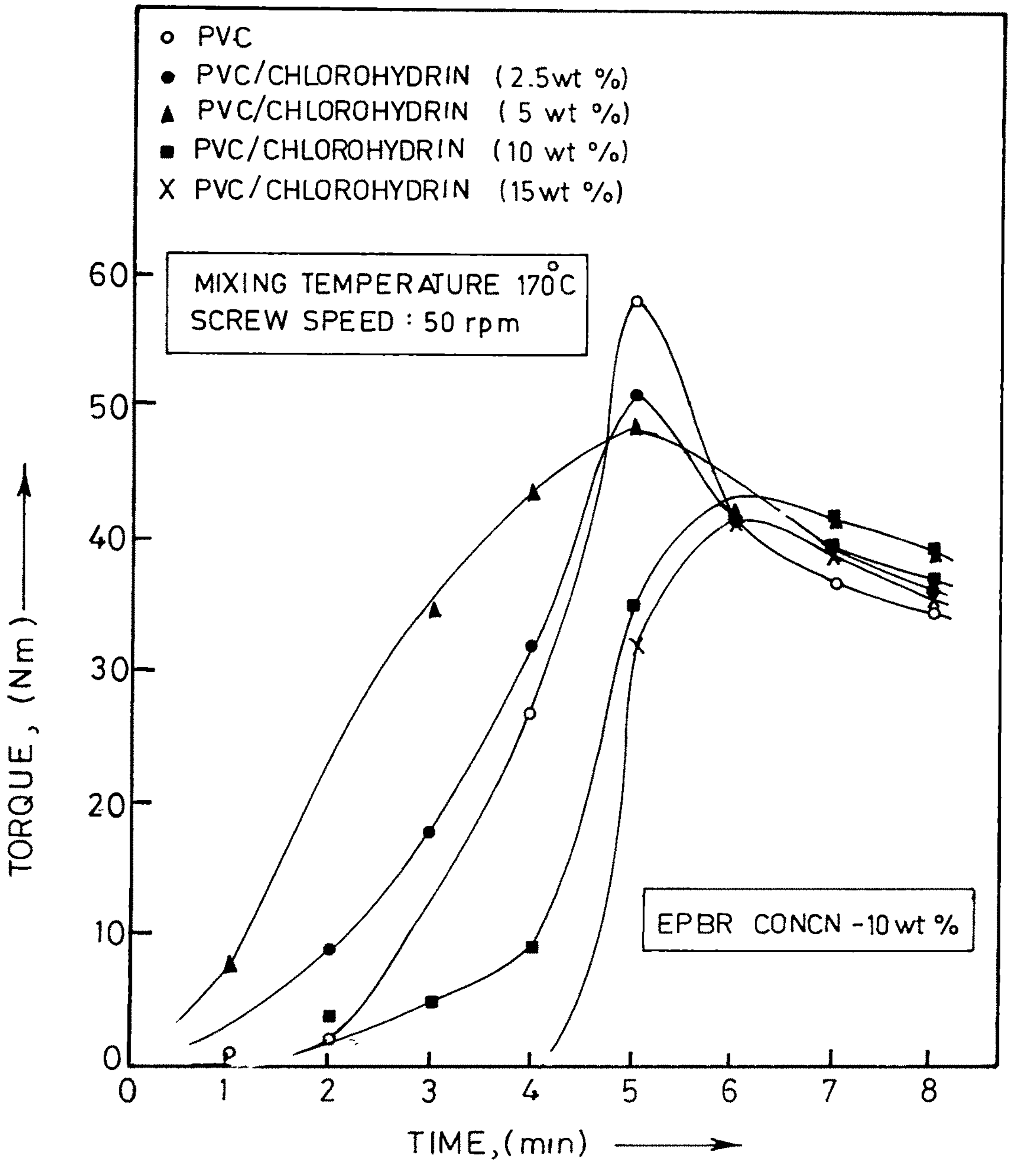


FIG3.8. MIXING TORQUE-TIME CURVES OF PVC AND ITS VARYING COMPOSITIONS OF PVC/CHLOROHYDRAIN BLENDS. WITH CHLOROHYDRIN IN DIFFERENT CONCENTRATIONS

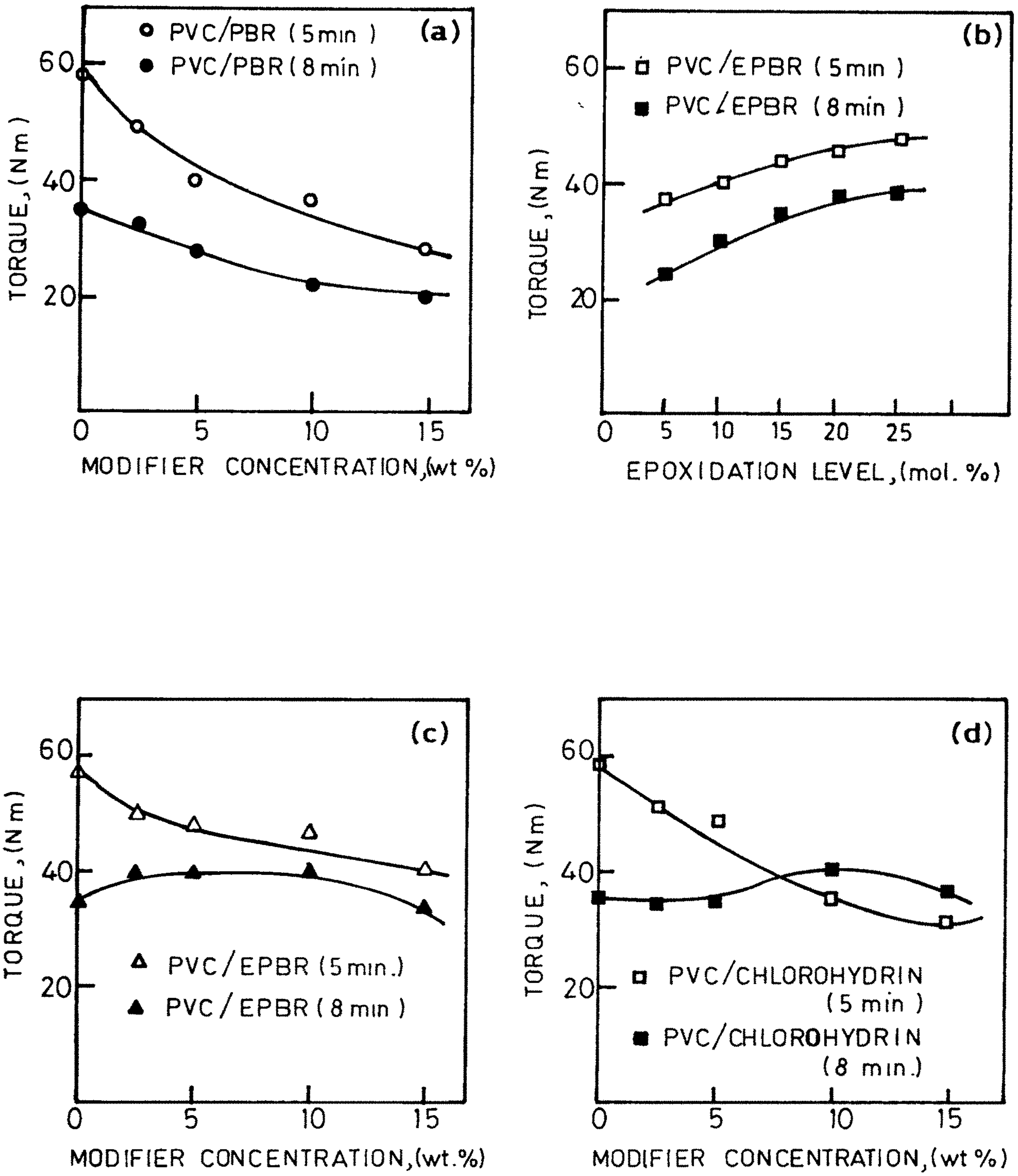


FIG 3.9. VARIATION OF TORQUE MAXIMUM (5min) AND TORQUE REGIME (8 min) OF PVC AND ITS BLENDS WITH DIFFERENT CONCENTRATIONS OF VARIOUS MODIFIERS. **(a)** PVC/PBR, **(b)** PVC/EPBR (10 wt %), **(c)** PVC/EPBR (25 mol. %), **(d)** PVC/CHLOROHYDRIN.

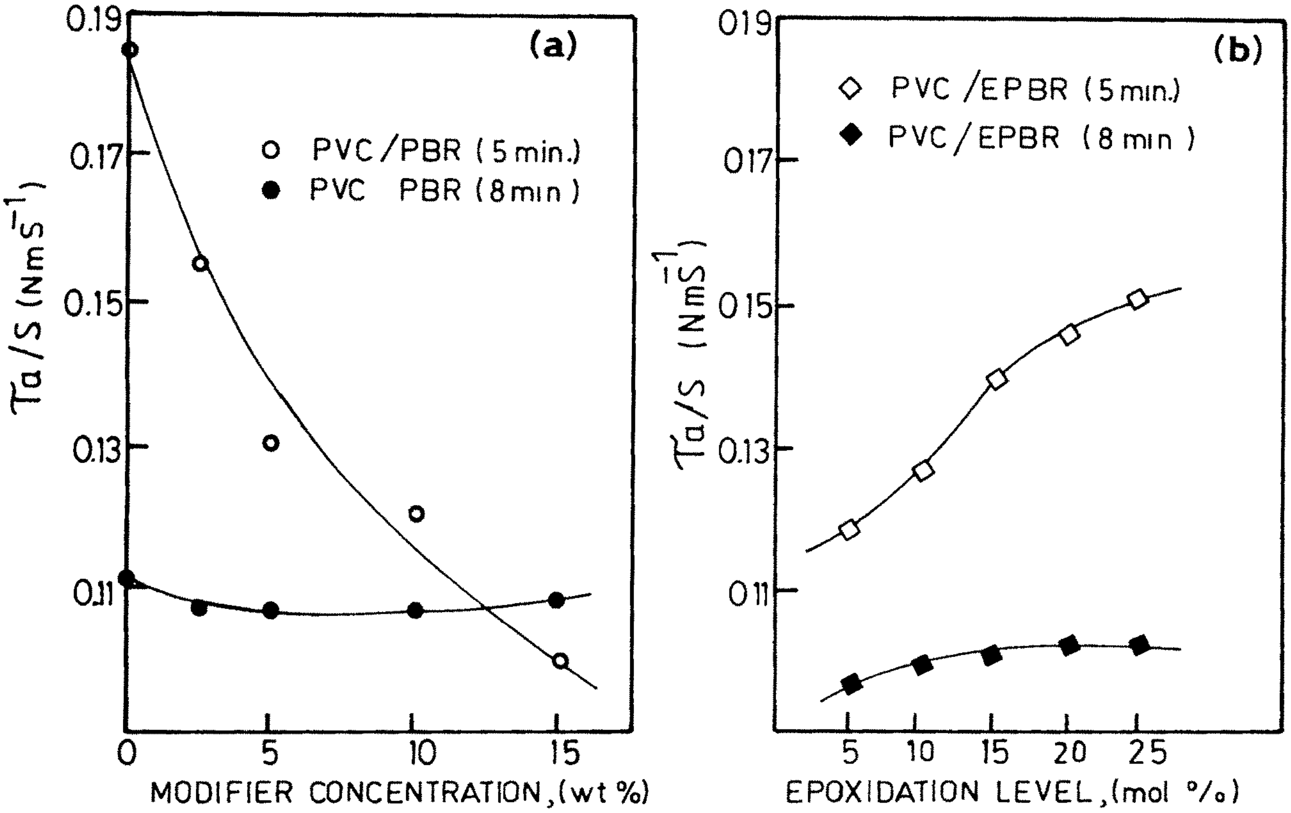


FIG. 3·10(a) VARIATION OF Ta/S VALUES OF PVC AND ITS BLENDS WITH DIFFERENT CONCENTRATIONS OF PBR

(b) VARIATION OF Ta/S VALUES OF PVC AND ITS BLENDS WITH EPBR OF DIFFERENT EPOXIDATION LEVEL

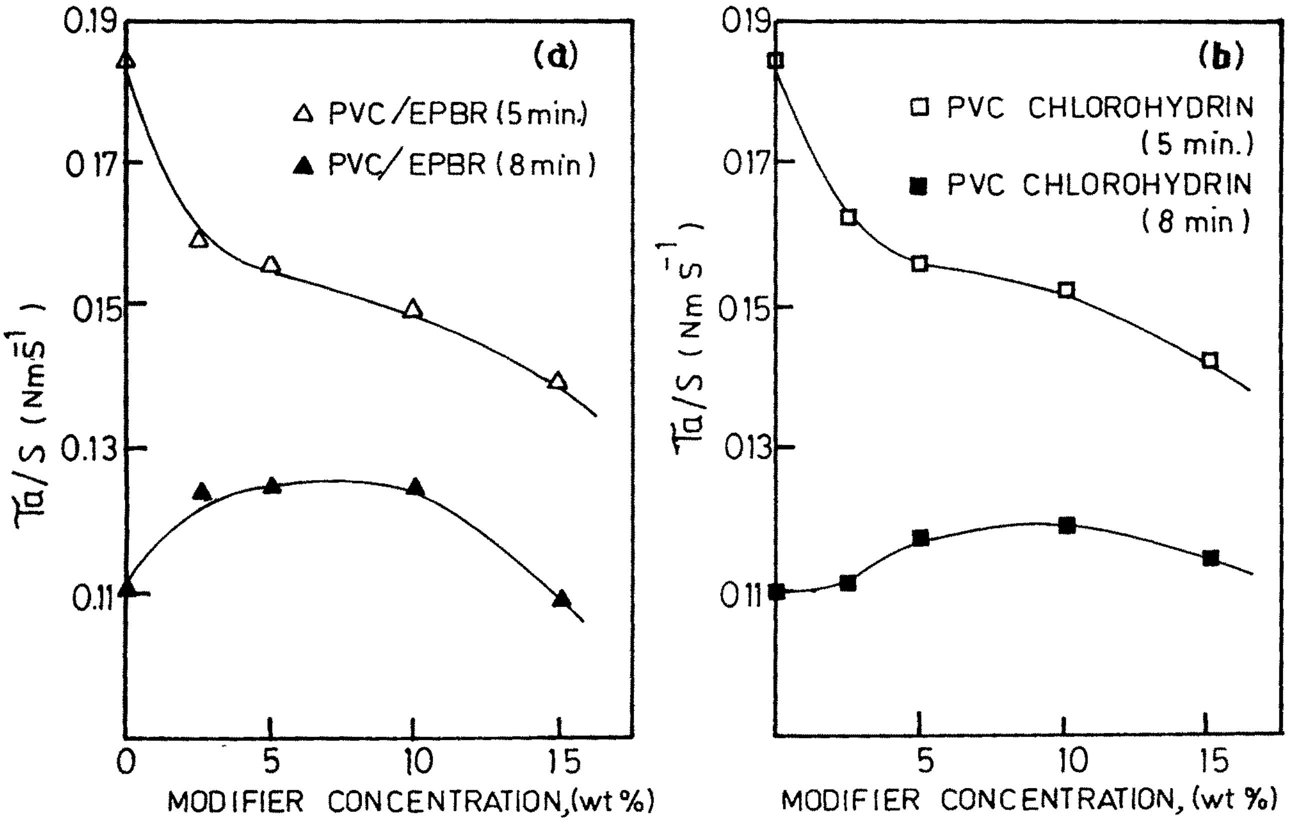


FIG.3·11(a) VARIATION OF Ta/S VALUES OF PVC AND ITS BLENDS WITH DIFFERENT CONCNS.OF EPBR (25 mol.%)

(b) VARIATION OF Ta/S VALUES OF PVC AND ITS BLENDS WITH DIFFERENT CONCNS OF CHLOROHYDRIN.

At higher concentrations of the rubbery phase, the rise in torque with time is slow and in some cases takes long time to reach maxima (Fig. 3.7-3.9). This may be ascribed to the lubrication action brought about by the rubbery phase at higher concentrations and/or incomplete melting and fusion of PVC particles. These observations show the importance of suitable blending conditions to ensure satisfactory degree of blending within a reasonable time without degradation.

From the Fig. 3.6 it is evident that, in the case of PVC/EPBR blends (b_1 to b_5), the maximum torque developed increases with increasing degree of epoxidation. This is only to be expected from the Tg of the added rubbery phase which increases with the increasing epoxidation level. This may also suggest some interaction between the two components involving epoxy groups .

Goodrich and Porter[14] and later Das[15] proposed a method in which mixing torques obtained from a Brabender plastograph can be converted into standard rheological properties using the following equations :

$$\eta_a = \sigma_a/\tau_a = KT_a/K'S = QT_a/S \qquad \text{———(1)}$$

$$\sigma_a = KT_a \quad ?$$

$$\gamma_a = K'S$$

$$S = 2\pi/60 \text{ x } R$$

$$Q = K/K'$$

η_a is the apparent shear viscosity, where σ_a is the apparent shear stress, τ_a is the apparent mixing torque measured, γ_a is the apparent shear strain rate, S is the angular rotor speed, R is the rotor speed used, and K and K' are the instrumental constants.

Equation (1) shows that τ_a/S is directly proportional to the apparent shear viscosity (i.e. apparent melt viscosity). Figure 3.10 shows the τ_a/S (apparent shear viscosity) at 5 min (corresponding to maxima in most cases) and torque regime (at 8 min) for various blends. The melt behaviour of the blends qualitatively follows that which one would ~~one~~ expect~~s~~ from the values of the components. For example, a rubbery phase with a lower Tg gives a lower blend viscosity at equivalent concentration. It is also clear from the plots that in the early stage transfacial blending helps the equipment to apply shear and the problem of shearing two liquids of different viscosity begins to be alleviated as the mixing proceeds; especially at lower concentration of the rubbery phase.

However, it should be remembered that the simple viscosity value is obviously an over simplification. Such factors as the effect of shear rate on viscosity, melt fracture, melt drawability and 'nerve' are very ~~may be~~ important. ~~depending on the type of fabrication equipment being used.~~

3.3.3 THERMAL ANALYSIS

Thermal Stability Studies on PVC Blends: PVC is an intrinsically thermally unstable polymer which owes its commercial success to the development of effective means of stabilisation. There is a good deal of evidence in the literature to the effect that incorporation of polymers containing highly polar groups into PVC tend to destabilize ~~the latter~~ PVC[16,17] whereas relatively non-polar polymers stabilize PVC[18].

In the present work, the thermal stability of the PVC blends ~~were~~ was investigated by HCl evolution technique and thermogravimetric analysis.

3.3.3.1 HCl evolution technique: When PVC is heated in an inert atmosphere, at first only HCl is given off with the onset of degradation resulting in the formation of polyene sequences, but later other degradation products are formed. The time taken for the initiation of degradation at constant temperature is called the induction time and hence, it can be used as an indication of thermal stability imparted to PVC by the various rubbery phases in the blends.

In this method, the polymer samples were heated at 190 ± 1°C and the degradation process was followed by monitoring the change in pH of the solution (in which the gaseous degradation products were absorbed) as a function of time (Fig. 3.12). The results obtained from such experiments are shown in (Fig. 3.13). It is evident from the figure that PVC/PBR blend (b_3) shows the highest induction time of 50 min followed by PVC/EPBR blend (c_3) with 40 min, which are both higher than that of neat PVC (30 min). The Higher induction time observed in these blends indicates that PBR

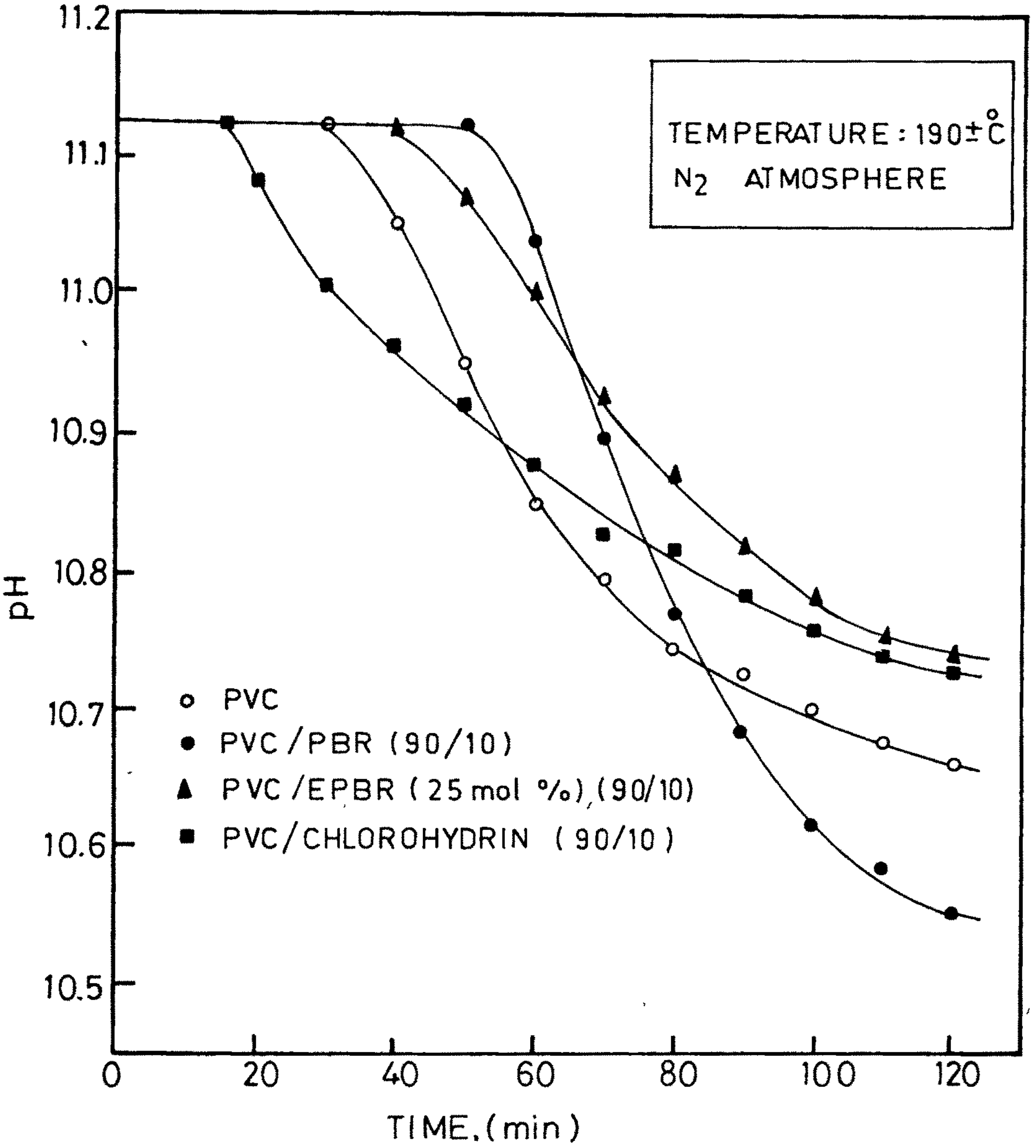


FIG 3.13 VARIATION OF pH IN THE DISSOLVING MEDIUM WITH DEGRADATION TIME FOR PVC AND ITS BLENDS.

and EPBR increase the inherent stability of PVC, by reducing the polar tensions within the PVC matrix[19,20]. Interestingly, PVC/EPBR blends show~~s~~ slower rates of degradation than PVC/PBR blend which points to the better long-term stability afforded to by EPBR than PBR. However PVC/chlorohydrin blend shows lowest induction time (15 min) points to poor long term stability.

3.3.3.2 Thermogravimetric analysis: A typical TGA plot of PVC exhibits two distinct portions. Once degradation has started, weight loss is rapid to about 50% weight loss. From 50 to 57 % the weight loss is gradual after which it is rapid again. As PVC contains about 58 weight% of HCl, the first decomposition stage is identified with the loss of HCl only. In the present study, the thermal characteristics were determined mainly based on first decomposition stage.

Nonsense

Think

PVC does not contain any HCl.

Heating

TGA of PVC and its blends ~~were~~ was carried out in an N_2 atmosphere up to 450°C and the thermograms obtained are shown in (Fig. 3.14, 3.15). The ~~I~~initial degradation temperature (IDT) and other thermal characteristics determined from these plots are given in Table 3.6.

Under the given experimental conditions IDT of neat PVC is approximately 240°C which changes upon incorporation of various rubbery phases. At equivalent concentration, EPBR (blend C_3, IDT 320°C) imparts better thermal stability to PVC than PBR (blend a_3, IDT 260°C) whereas chlorohydrin incorporation has no effect on IDT (blend d_3, IDT 240°C).

Table 3.6

Thermal characteristics of PVC and its blends.

Blend code	IDT °C	T_{10} °C	T_{30} °C	T_{50} °C	Activation energy* KJ mol^{-1} (1st transition)
p	240	360	380	410	205.70
a_3	260	370	388	445	208.68
c_1	240	370	400	445	-
c_2	270	380	400	452	-
c_3	320	385	415	580	241.48
c_4	320	380	405	588	-
d_3	240	372	410	490	212.85

IDT - Initial Decomposition Temperature

T_{10} - Temperature at which 10% wt loss

T_{30} - Temperature at which 30% wt loss

T_{50} - Temperature at which 50% wt loss

* In presence of 1.5 phr. OTM.

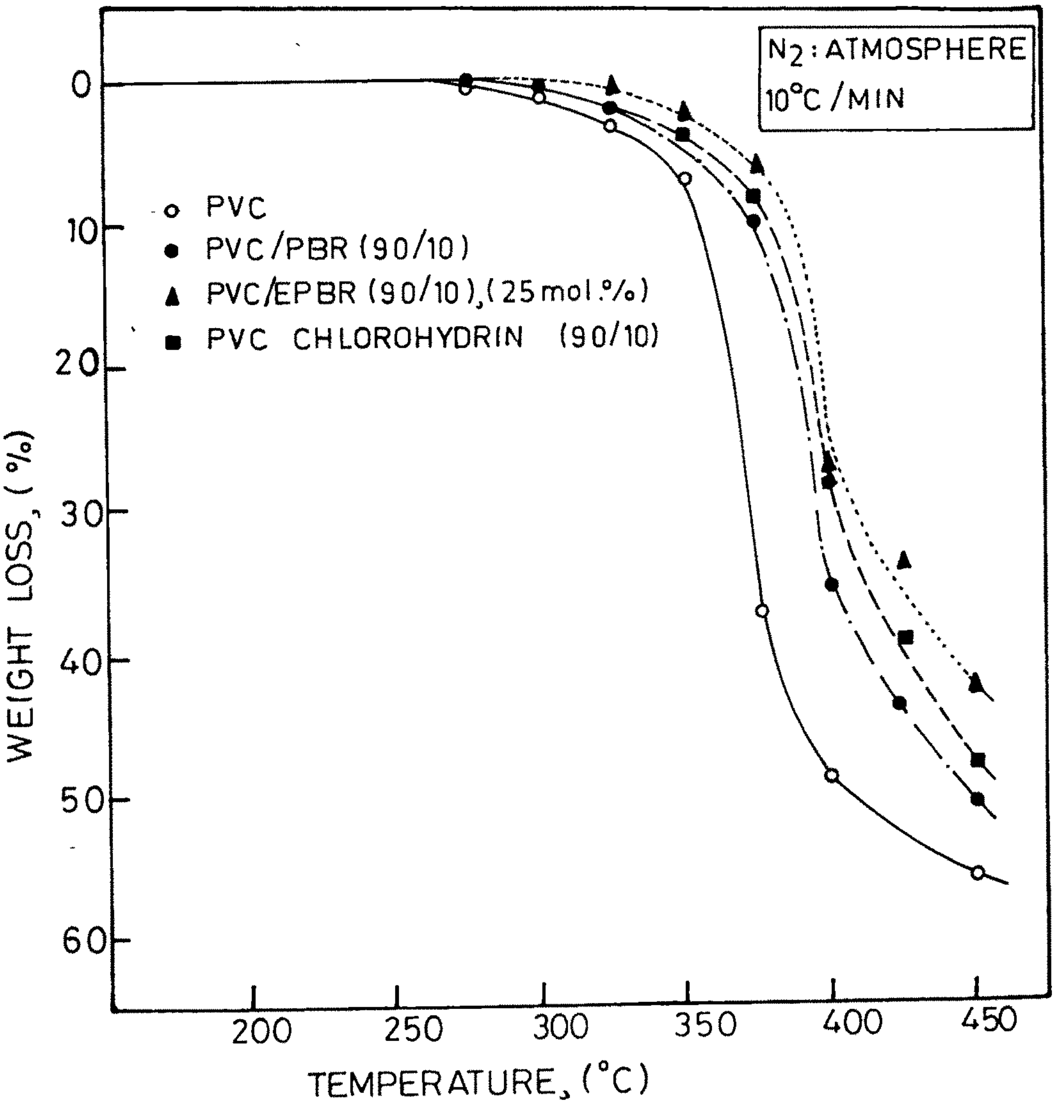


FIG 3 14 TGA THERMOGRAMS OF PVC AND ITS BLENDS WITH DIFFERENT MODIFIERS

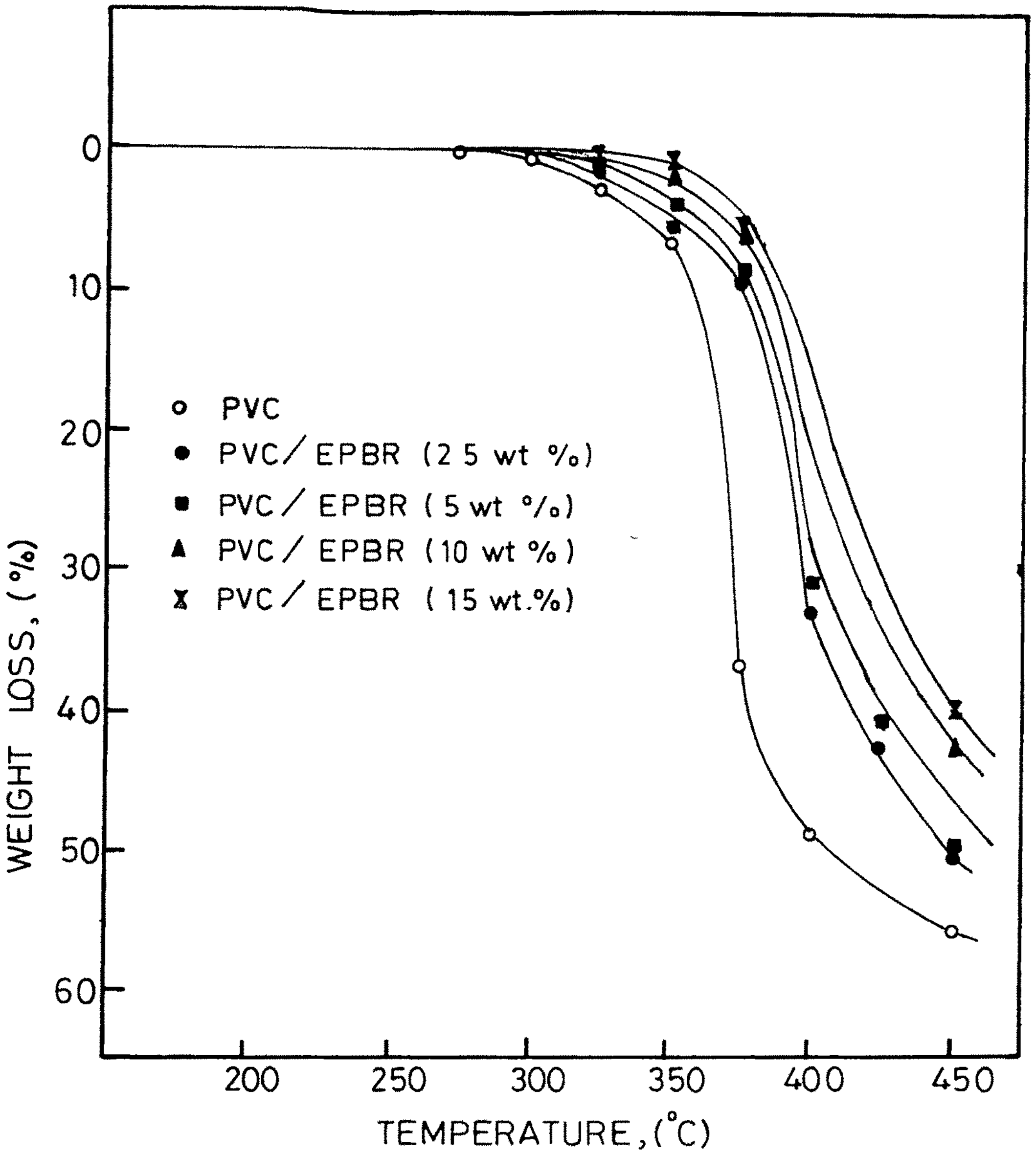


FIG.3.15. TGA THERMOGRAMS OF PVC AND ITS BLENDS WITH DIFFERENT CONCENTRATIONS OF EPBR (25 mol %)

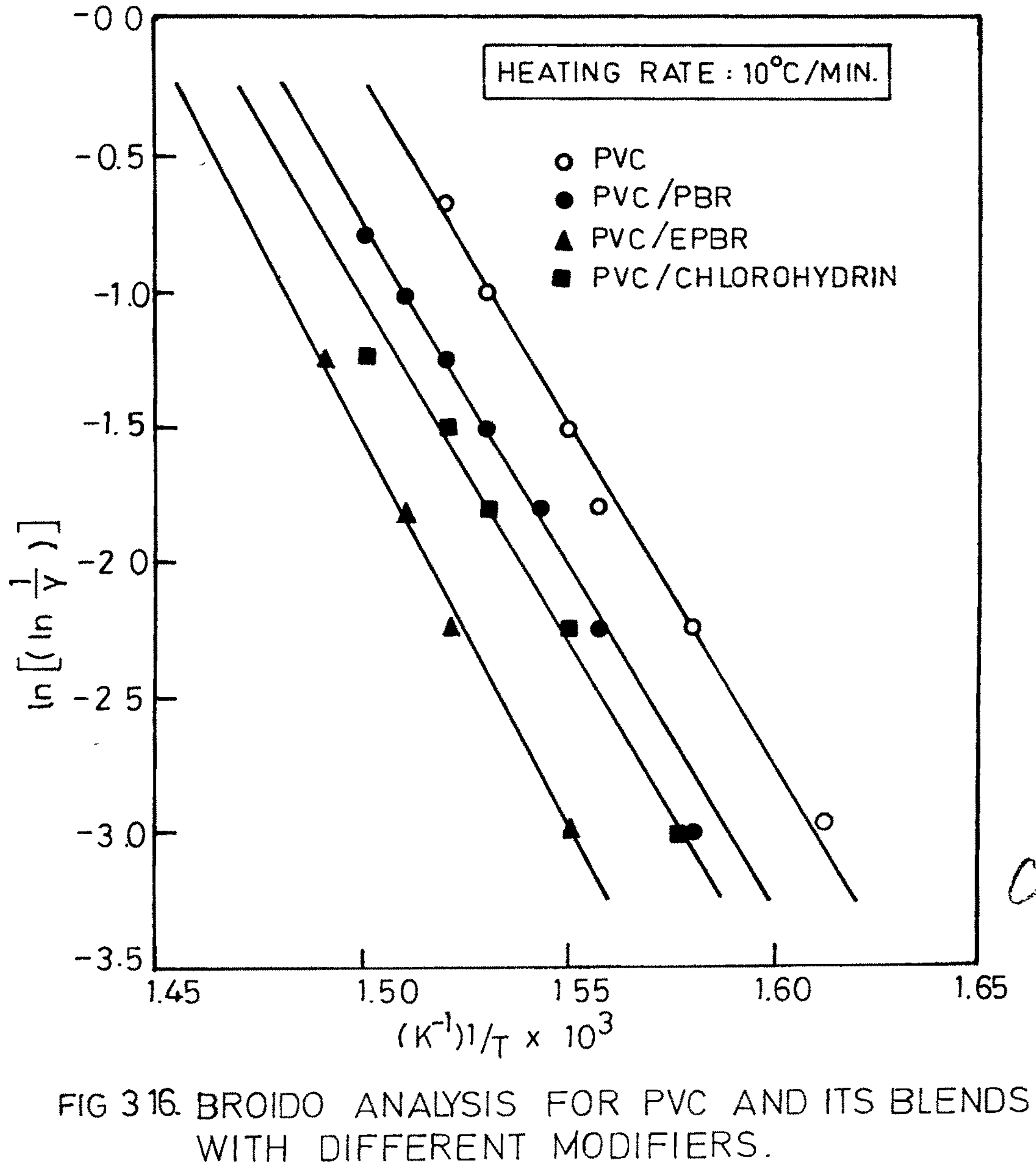


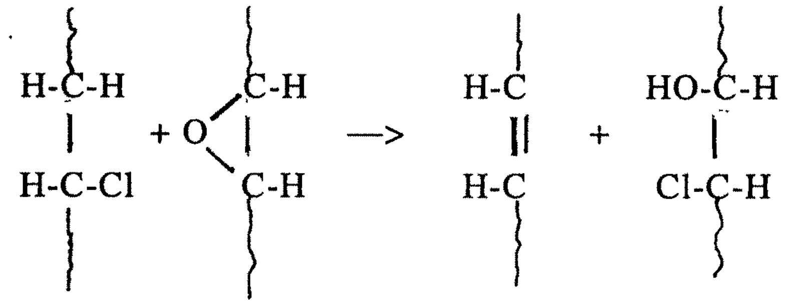
FIG 3 16. BROIDO ANALYSIS FOR PVC AND ITS BLENDS WITH DIFFERENT MODIFIERS.

Good

Also IDT increases with the increase in the concentration of EPBR in the blend (c_1, c_2, c_3, c_4).

The above results indicate that the thermal stability of PVC improves significantly with EPBR incorporation. This may be ascribed to the ability of epoxy groups of EPBR to undergo a ring-opening reaction with the HCl evolved from the PVC backbone as shown below. Absorption of HCl prevents it from bringing about further degradation. ?

Why absorption?



This mechanism is similar to the one proposed in the case of PVC/PBR solution blends[21]. The Chlorohydrin derivative itself, on the other hand, does not improve the thermal stability because it ~~may not be~~ is not as effective as PBR and EPBR in removing HCl. Modification of EPBR during degradation brings about similarity in behaviour in PVC/EPBR and PVC/chlorohydrin blend beyond a certain extent of degradation. Evidence for the modification of EPBR comes from the IR spectral analysis of PVC/EPBR blends prepared by melt mixing (see 3.3.4).

Analysis of thermograms using the method developed by Broido allows the activation energy associated with thermal breakdown to be calculated[22]. The integrated Broido equation required to calculate activation energies is of the form.

$$\ln[\ln(1/y)] = -(E/R)\,(1/T) + \text{constant}$$

K

where y is the weight of the original material taking part in a given reaction step, E is the activation energy of thermal breakdown, R is the gas constant (8.314 J k^{-1} mol^{-1}) and T is the absolute temparature. A plot of $\ln[\ln(1/y)]$ against 1/T should yield a line of slope -E/R for a first order reaction. Such plots for PVC and its various blends are given in (Fig. 3.16).

The activation energy for heat degradation of PVC and its blends calculated from the above plots are given in Table 3.6. The higher energy of activation observed in the case of PVC/EPBR blend (90:10)(c_3) indicates that EPBR makes a positive contribution towards the thermal stability of PVC. In the case of other blends, the change in activation energy is only marginal which shows that there is no significant improvement in thermal stability of PVC.

3.3.4 MICROSTRUCTURAL STUDIES

3.3.4.1 Fourier Transform Infra Red Spectroscopy (F.T.I.R)

Information regarding the possible interaction between the components in a polymer blend can be obtained by comparison of the infra red spectra of the individual components with that of the blend[23,24].

FTIR spectra of neat PVC(P) and the PVC/PBR (a_3) and PVC/EPBR (c_3) blends are given in (Fig.3.17-3.19), and ? respectively. The spectrum of X c_3 exhibits a broad band between 3200-3600 cm^{-1} corresponding to hydrogen bonded hydroxyl group. This band is absent in the spectrum of PVC as well as EPBR, the two components from which the blend is prepared. The hydroxyl functionality is probably generated during the preparation of the blend by melt mixing process. Small amounts of HCl are evolved due to slight degradation of PVC during melting, apart from getting added on to the double bonds, reacts with the epoxy groups of EPBR forming the chlorohydrin derivative in situ. This is supported by the fact that infra red spectra of PVC/EPBR (c_3) and PVC/chlorohydrin (d_3) (Fig. 3.20) are similar. Such a reaction is adventageous in two ways : first, the efficient absorption ? of HCl prevents it from catalysing further degradation of PVC and second, generation of chloro and hydroxyl groups on EPBR backbone leads to better interaction and a certain degree of compatibility with PVC. These effects are reflected in the improvement in the thermal stability of PVC with the incorporation of EPBR[21]. For the same

How is the word Absorption
being used here?

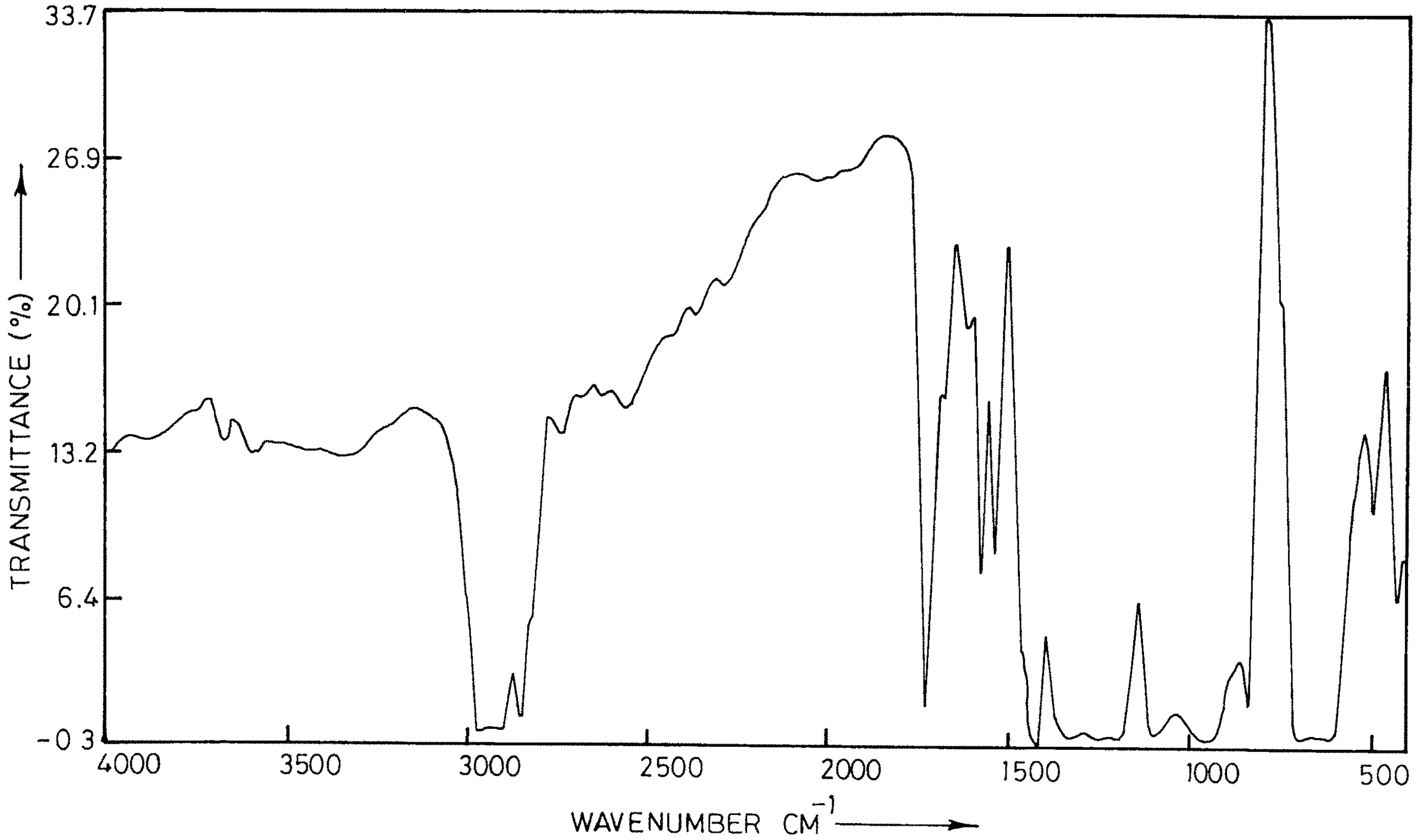


FIG 217 FT-IR SCAN OF PVC (P)

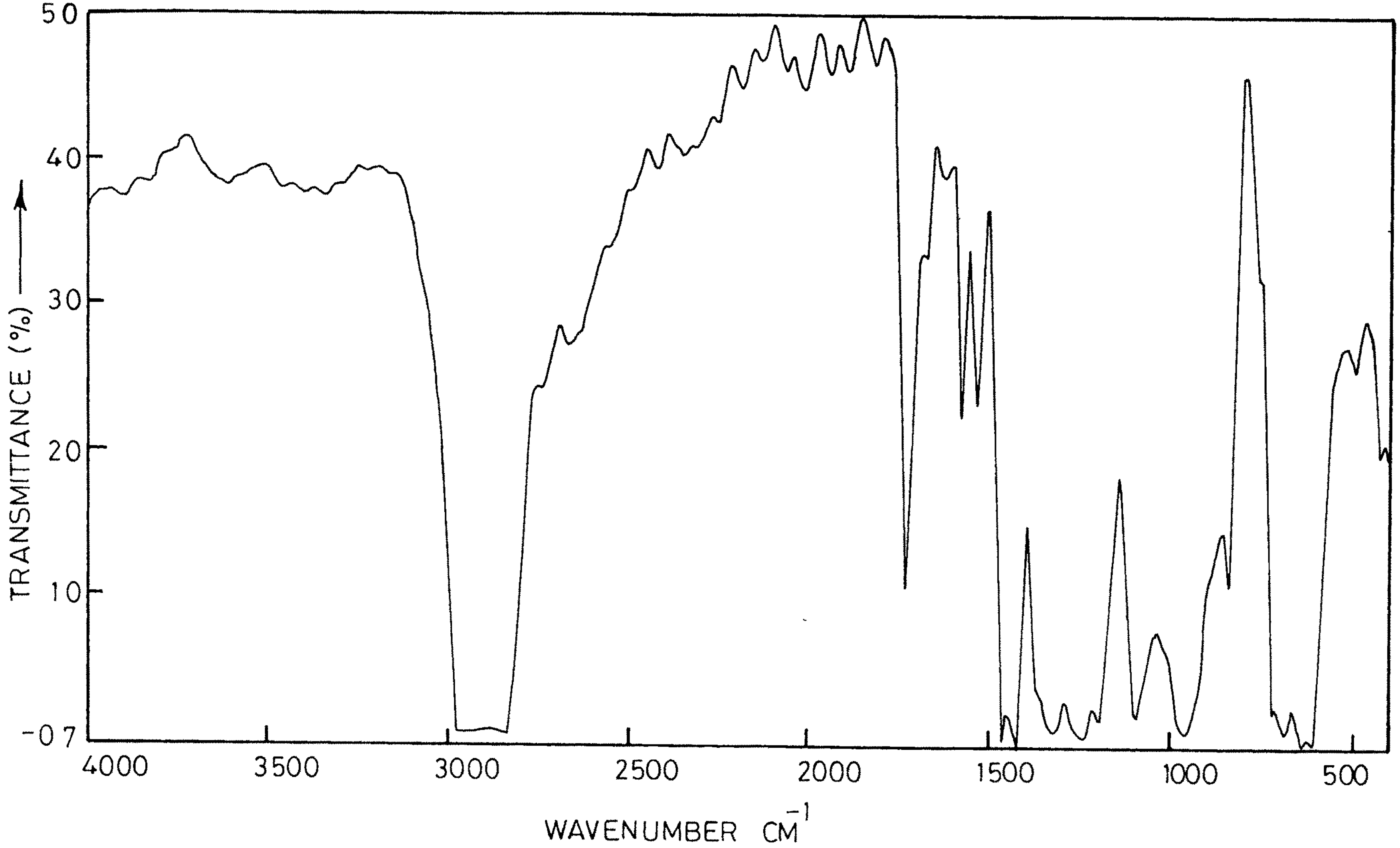


FIG 318 FT-IR SCAN OF PVC/PBR (90/10) BLEND (a_3)

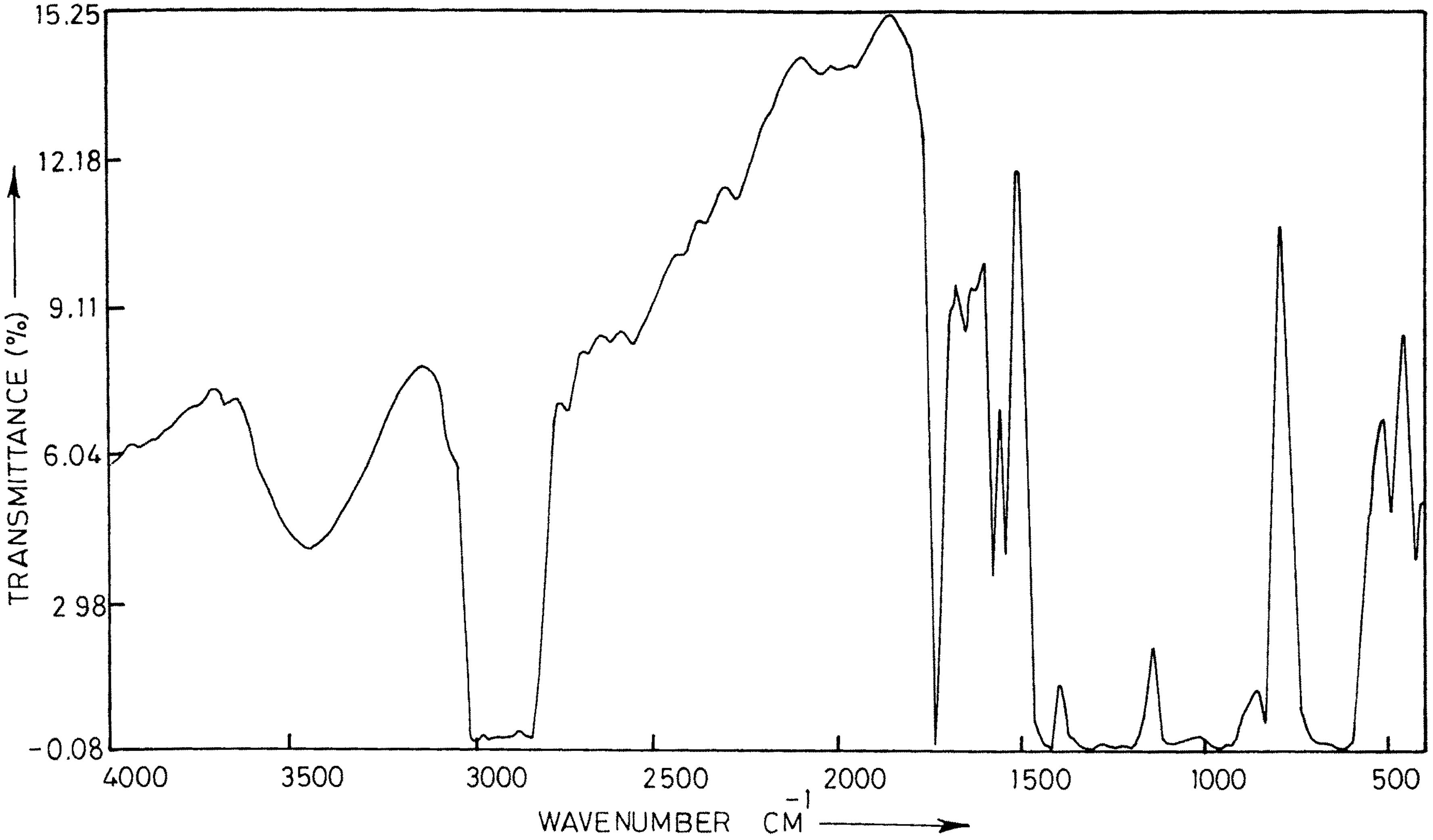


FIG 3 19 FT-IR SCAN OF PVC/EPBR (90/10) BLEND (C_3)

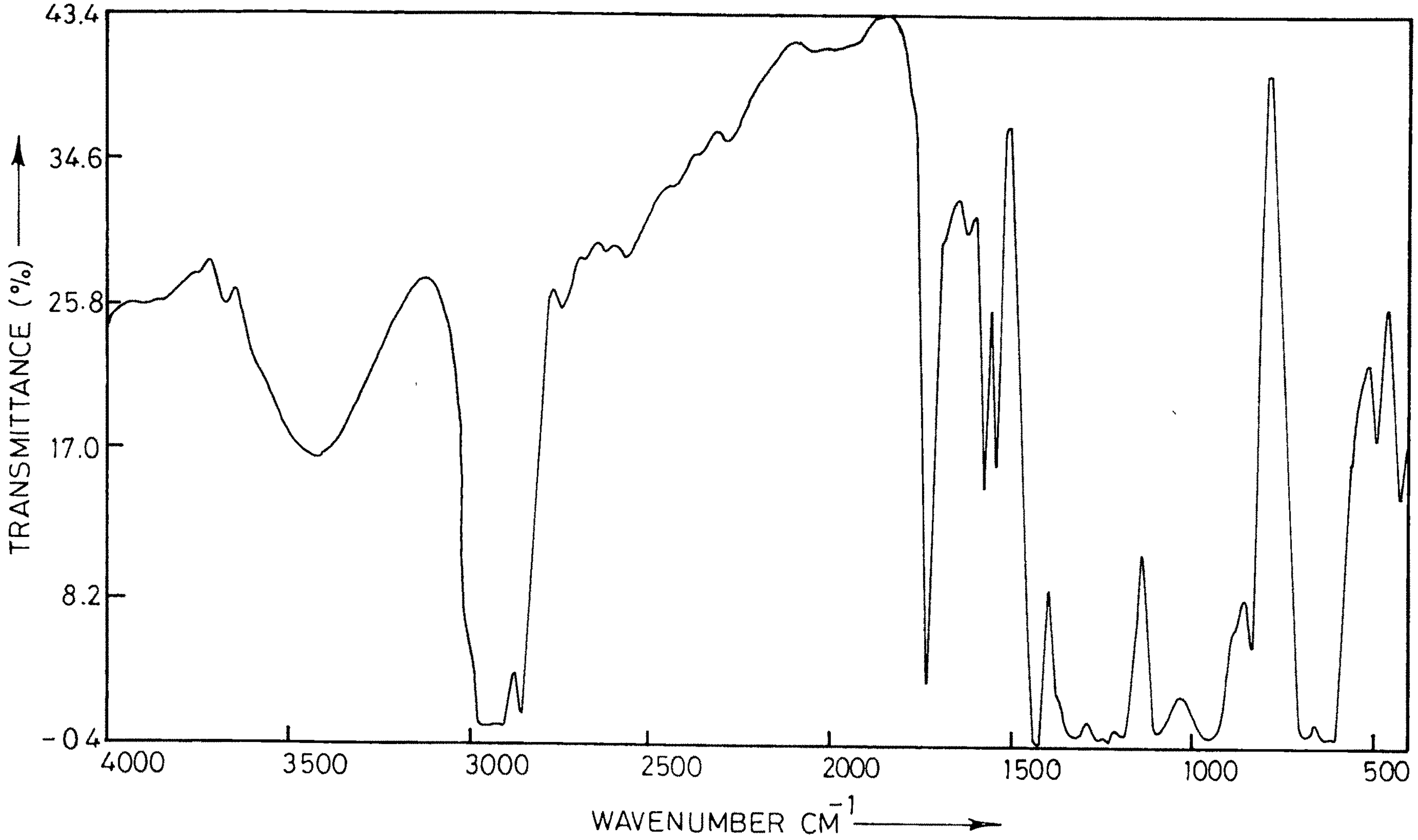


FIG 3 20 FT- IR SCAN OF PVC/CHLOROHYDRIN (90/10) BLEND (d3) reasons, these blends are expected to show improvement in ceratin mechanical properties.

PVC/PBR (a_3) spectrum does not exhibit any new band (Fig.3.19), because addition of HCl to the double bonds of PBR has no effect on infra red spectrum of blend.

Odd ?

logic lacking

3.3.4.2 Scanning Electron Microscopy (SEM)

Scanning electron micrographs of the Izod impact fractured surfaces of the samples of PVC and blends are shown in (Fig. 3.21-3.24), which show more or less uniform dispersion of the rubbery phase in the blends. The fractured surface of PVC (Fig. 3.21a, 3.22a) appears to be brittle and so is the case with PVC/PBRblends b_3(Fig. 3.21b, 3.22b). For rather obvious reasons, PVC does not adhere well to PBR and therefore, addition of PBR does not alter the nature of PVC. On the other hand, the fractured surface of PVC/EPBR(c_3) (Fig. 3.21c, 3.22c) and PVC/chlorohydrin(d_3) (Fig. 3.21d, 3.22d), blends appear to be rough. This may be due to the increased adhesion between the components of these blends which transform a brittle fracture into a ductile fracture. Effect of various composition of PVC/EPBR(25 mol%) blends can be seen in (Fig. 3.23, 3.24).

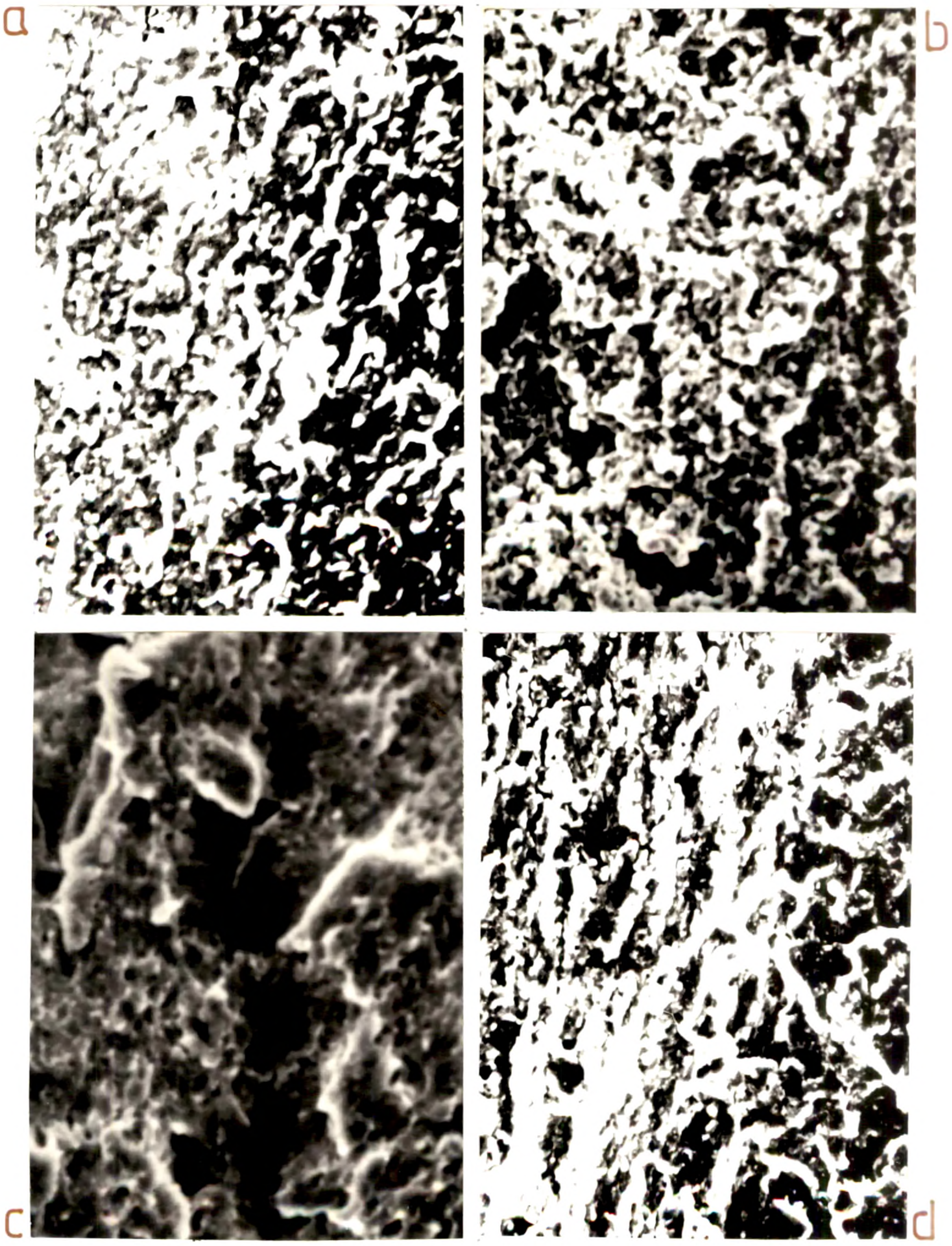
Speculation ?

With the increase in the amount of rubbery phase in the PVC/EPBR blends phase seggregation slowly sets in, with the consequent increase in brittleness again as shown by the micrographs (Fig. 3.23d, 3.24d) c_4 (15

X

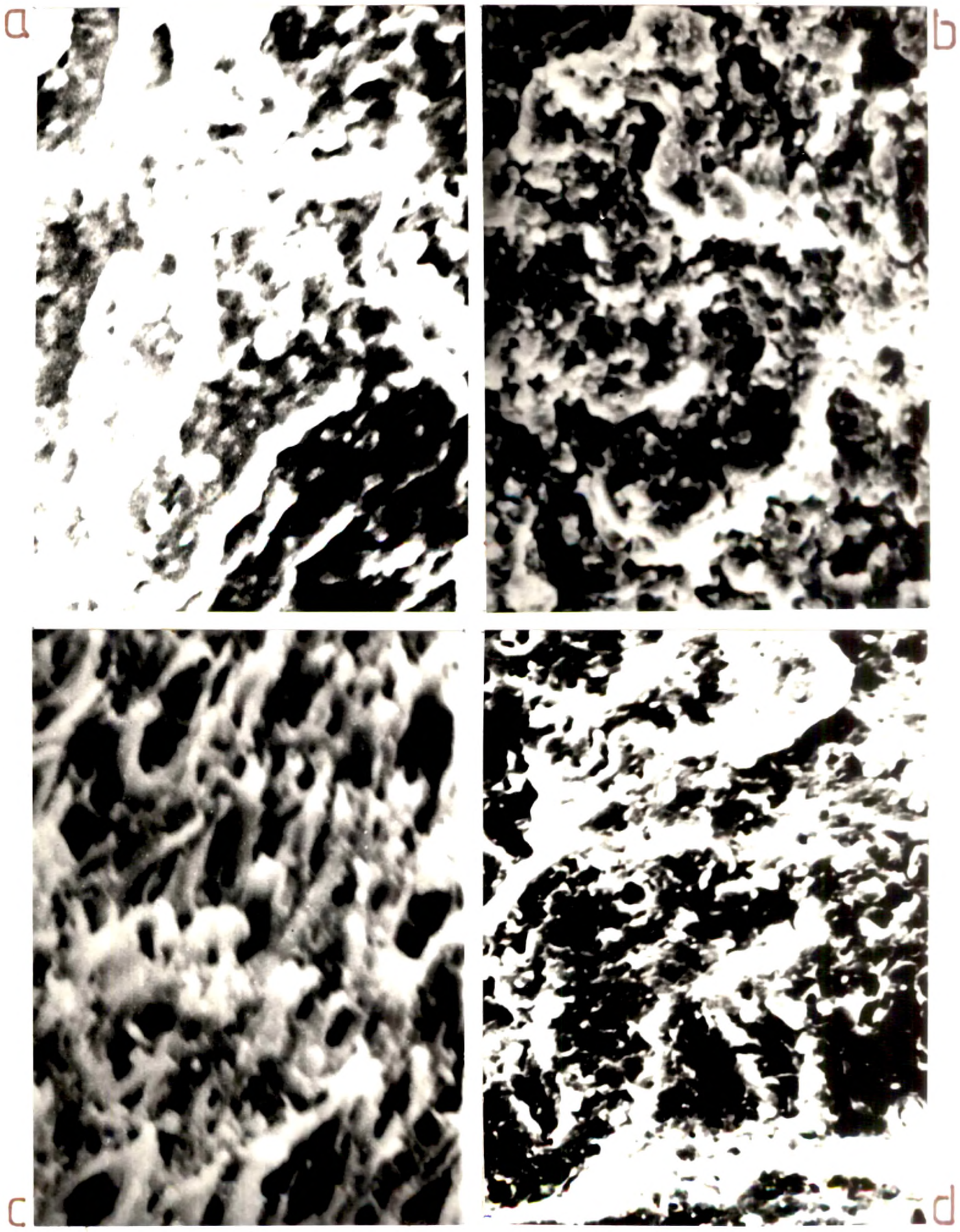
3.21 SEM micrographs of the Izod impact fractured surface of

(a) PVC(P) and its blends **(b)** a_3, **(c)** c_3, **(d)** d_3 (X 1650).

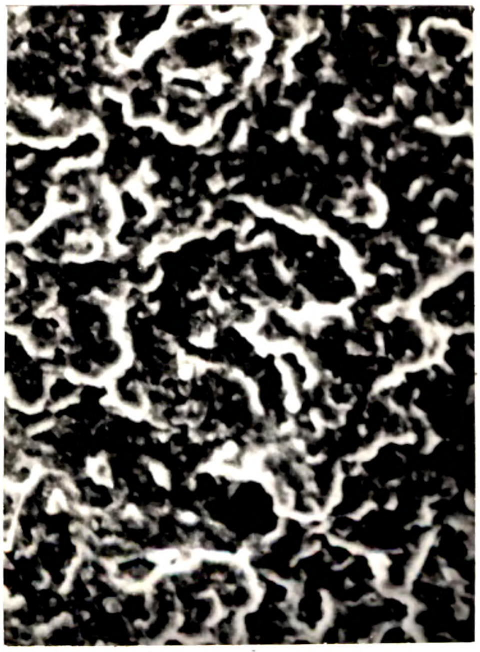

a
b
c
d

3.22 SEM micrographs of the Izod impact fractured surface of

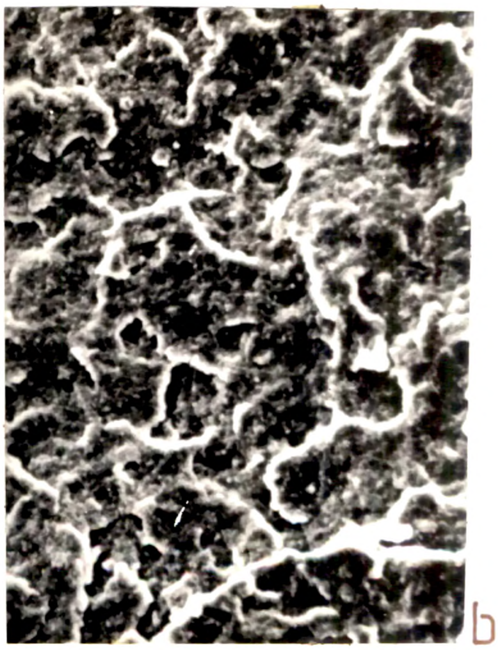
(a) PVC(P) and its blends **(b)** a_3, **(c)** c_3, **(d)** d_3 (X 3300).


a
b
c
d

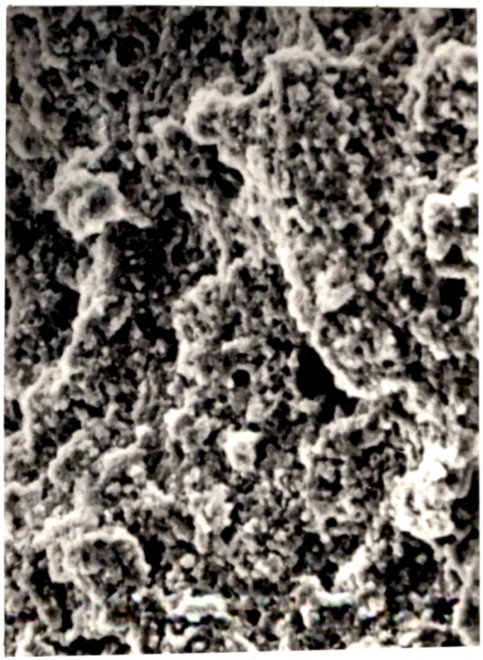
3.23 SEM micrographs of the Izod impact fractured surface of PVC blends **(a)** c_1, **(b)** c_2, **(d)** c_4 (X 1650).



a



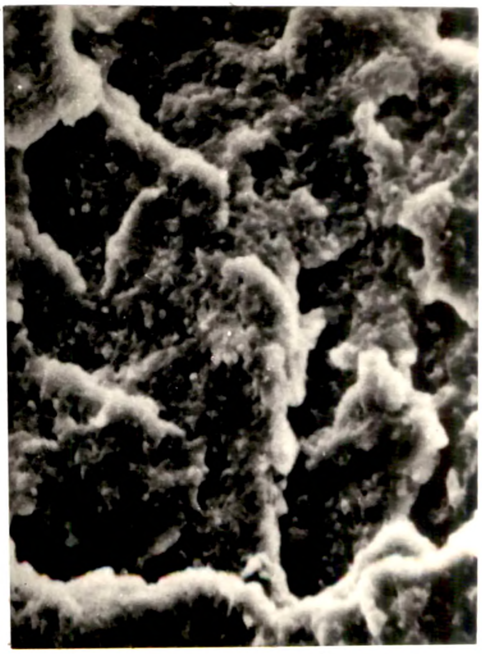
b



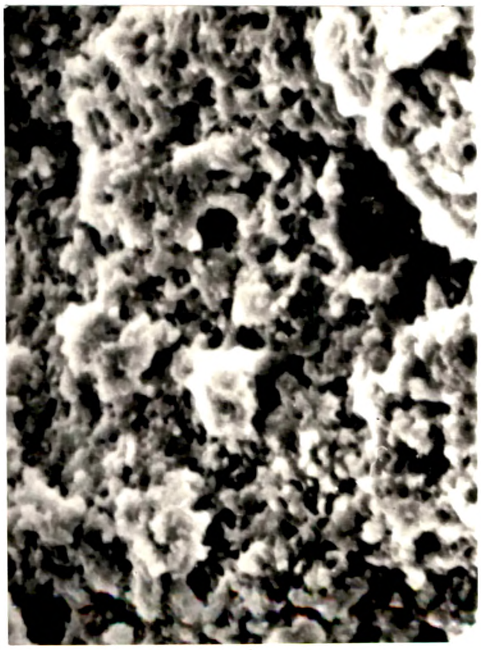
d

3.24 SEM micrographs of the Izod impact fractured surface of PVC blends **(a)** c_1, **(b)** c_2, **(d)** c_4 (X 3300).

a



b



d

wt% EPBR). Similarly fractured surfaces of PVC/EPBR (2.5 wt%) (c_1) and PVC/EPBR (5 wt%) (c_2) also do~~es~~ not show transformation of brittle to ductile behaviour, suggests EPBR concentrations in this blends are not sufficient for modification.

From the ductile fractured surfaces of the PVC/EPBR blends, it can be understood that the formation of such surfaces ~~are~~ is due to the higher energy absorption during impact fracture. This is well supported by the high impact strength shown by these blends (see. 3.3.5.3) at optimum concentration of the rubbery phase.

3.3.4.3 X-ray Diffraction

Qualitative information regarding the relative compatibility of the components in the blends can be obtained from the reduction in % crystallinity of PVC[25]. From the X-ray diffraction patterns given in (Fig. 3.25) it can be seen that by incorporation of PBR in PVC, the intensities of the peaks are not altered much whereas EPBR and chlorohydrin derivatives lead to noticeable decreases in intensities. This suggests that loss in crystallinity is higher in the latter case because of better interaction between the components. Therefore, these blends not only show better thermal stability, they are expected to show improvement in certain mechanical propeties as well.

3.3.5 PERFORMANCE PROPERTIES

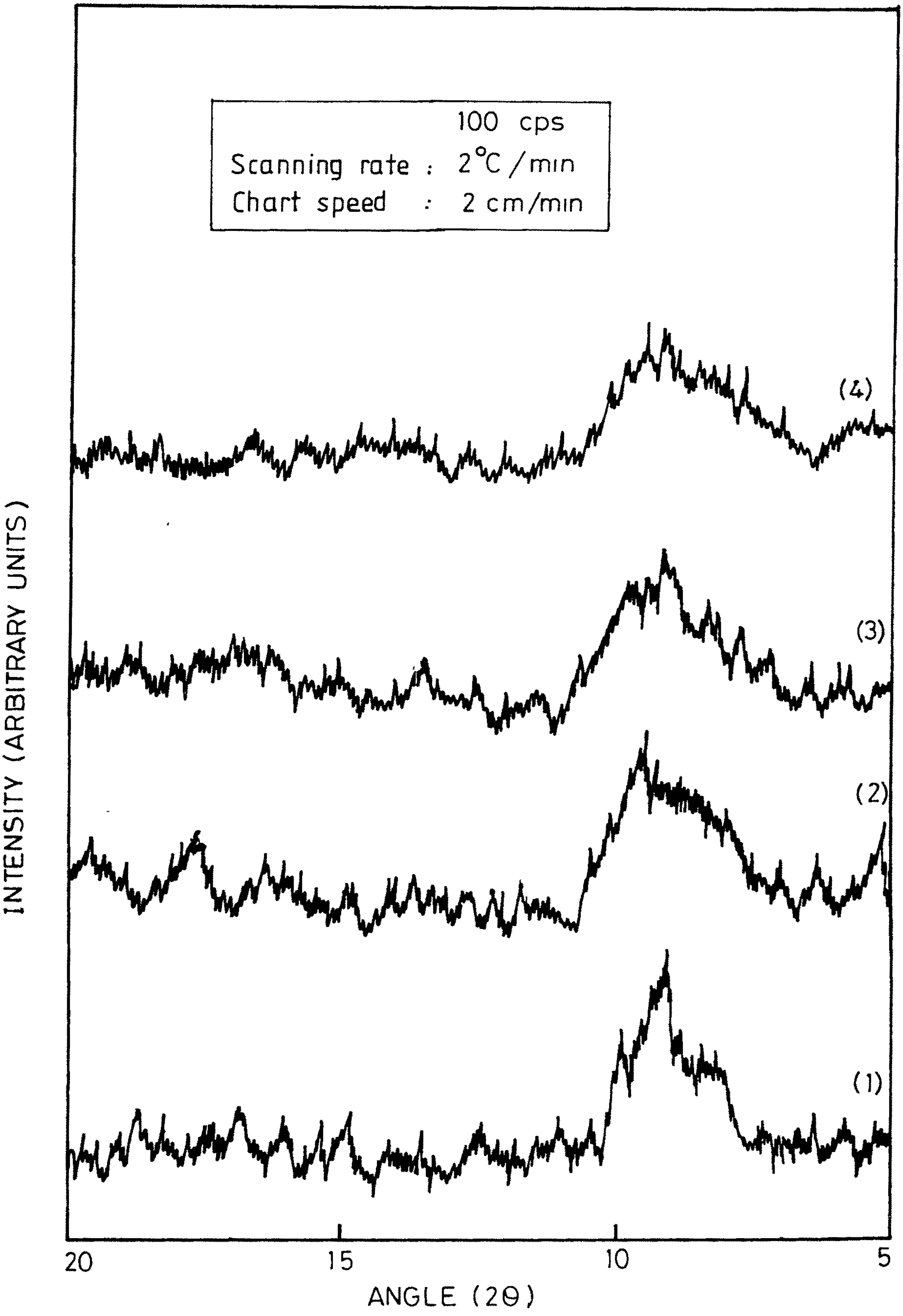


FIG.3.25. X-RAY DIFFRACTION PATTERN OF PVC AND ITS BLENDS
(1) PVC (P), (2) PVC/PBR (90/10) a_3, (3) PVC /EPBR (90/10) C_3
(4) PVC/CHOLOROHYDRIN (90/10) d_3

3.3.5.1 Tensile properties:

The tensile properties of PVC and its blends with PBR, EPBR, and chlorohydrin are summarized in Tables 3.7-3.10. Figure 3.26 illustrates the influence of different modifiers at various concentrations on the tensile strength. From this (Fig. 3.26) it is clear that in the case of PVC/PBR blends the tensile strength of PVC decreases with the increase in PBR concentration. On the other hand, the loss is not so significant in the case of chlorohydrin modification. Effect of EPBR is intermediate between that of PBR and chlorohydrin.

The tensile moduli of the PVC blends are given in (Fig. 3.27). Here also increasing concentration of PBR significantly reduces the moduli of PVC blends. While chlorohydrin shows minimum loss in modulus and EPBR shows the intermediate effect.

Figure 3.28 and 3.29 illustrate effect of degree of epoxidation on the tensile strength and tensile modulus of PVC blends with constant EPBR concentration (10 wt%). It is clear that for the given concentration of EPBR the tensile strength of the blends increases as the epoxidation level increases upto 25 mol%. Effect of EPBR samples with higher degree of epoxidation (>25 mol%) were not investigated because of two reasons : first, under the preparative conditions employed, the samples showed gelation due to cross linking; second, higher Tg of these samples lead to higher mixing torques.

Table 3.7
Mechanical properties of PVC/PBR blends

Property	Test	PBR concentration, (Wt %)				
		0	2.5	5	10	15
Tensile strength 10^2 (Kg/cm^2)	ASTM D:638	4.68	3.89	3.12	2.47	1.70
Tensile Modulus 10^3 (Kg/cm^2)	ASTM D:638	17.10	16.60	15.80	14.40	12.20
Flexural strength 10^2 (Kg/cm^2)	ASTM D:790	8.87	8.57	7.83	7.57	6.51
Flexural Modulus 10^3 (Kg/cm^2)	ASTM D:790	35.03	33.28	31.85	29.49	25.53
Impact Strength Kg-cm/cm	ASTM D:256	3.10	2.60	1.70	1.20	1.10
Heat Deflection Temperature (°C)	ASTM D:648	68.0	67.50	67.00	66.00	64.00
Rockwell Hardness (R units)	ASTM D:785	118.00	115.00	110.00	99.00	80.00

kg not Kg

Table 3.8

Mechanical properties of PVC/EPBR (90/10) blends (b_1-b_5)

Property	Test	Epoxidation level, (Mol %)				
		5 (b_1)	10 (b_2)	15 (b_3)	20 (b_4)	25 (b_5)
Tensile strength 10^2 (Kg/cm^2)	ASTM D:638	2.40	2.80	3.20	3.60	3.80
Tensile Modulus 10^3 (Kg/cm^2)	ASTM D:638	12.10	12.50	13.60	14.10	15.20
Flexural strength 10^2 (Kg/cm^2)	ASTM D:790	5.50	5.80	6.52	7.30	7.57
Flexural Modulus 10^3 (Kg/cm^2)	ASTM D:790	24.58	24.80	25.53	27.37	30.16
Impact Strength Kg-cm/cm	ASTM D:256	2.40	3.60	16.00	23.90	30.17
Heat Deflection Temperature (°C)	ASTM D:648	66.00	66.50	67.00	67.50	67.50
Rockwell Hardness (R units)	ASTM D:785	98.00	99.00	103.00	104.00	105.00

Table 3.9
Mechanical properties of PVC/EPBR (25 mol%) blends

Property	Test	EPBR concentration, (Wt %)				
		0 (P)	2.5 (c 1)	5 (c 2)	10 (c 3)	15 (c 4)
Tensile strength 10^2 (Kg/cm^2)	ASTM D:638	4.68	3.98	3.90	3.89	3.10
Tensile Modulus 10^3 (Kg/cm^2)	ASTM D:638	17.18	16.68	16.20	15.20	13.80
Flexural strength 10^2 (Kg/cm^2)	ASTM D:790	8.87	8.58	7.92	7.57	6.57
Flexural Modulus 10^3 (Kg/cm^2)	ASTM D:790	35.03	33.25	30.85	30.16	23.88
Impact Strength Kg-cm/cm	ASTM D:256	3.10	5.00	16.00	30.17	16.30
Heat Deflection Temperature (°C)	ASTM D:648	68.00	67.50	67.00	66.50	65.00
Rockwell Hardness (R units)	ASTM D:785	118.00	115.00	112.00	105.00	97.00

Table 3.10

Mechanical properties of PVC/Chlorohydrin blends

Property	Test	Chlorohydrin, (Wt %)				
		0 (P)	2.5 (d_1)	5 (d_2)	10 (d_3)	15 (d_4)
Tensile strength 10^2 (Kg/cm^2)	ASTM D:638	4.68	4.18	3.92	3.98	3.52
Tensile Modulus 10^3 (Kg/cm^2)	ASTM D:638	17.10	16.90	16.20	15.80	14.20
Flexural strength 10^2 (Kg/cm^2)	ASTM D:790	8.87	9.00	8.28	7.80	7.20
Flexural Modulus 10^3 (Kg/cm^2)	ASTM D:790	35.03	36.68	33.52	30.90	23.10
Impact Strength Kg-cm/cm	ASTM D:256	3.10	6.10	19.90	35.30	25.70
Heat Deflection Temperature (°C)	ASTM D:648	68.00	67.50	68.50	69.00	67.00
Rockwell Hardness (R Units)	ASTM D:785	118.00	117.00	115.00	110.00	108.00

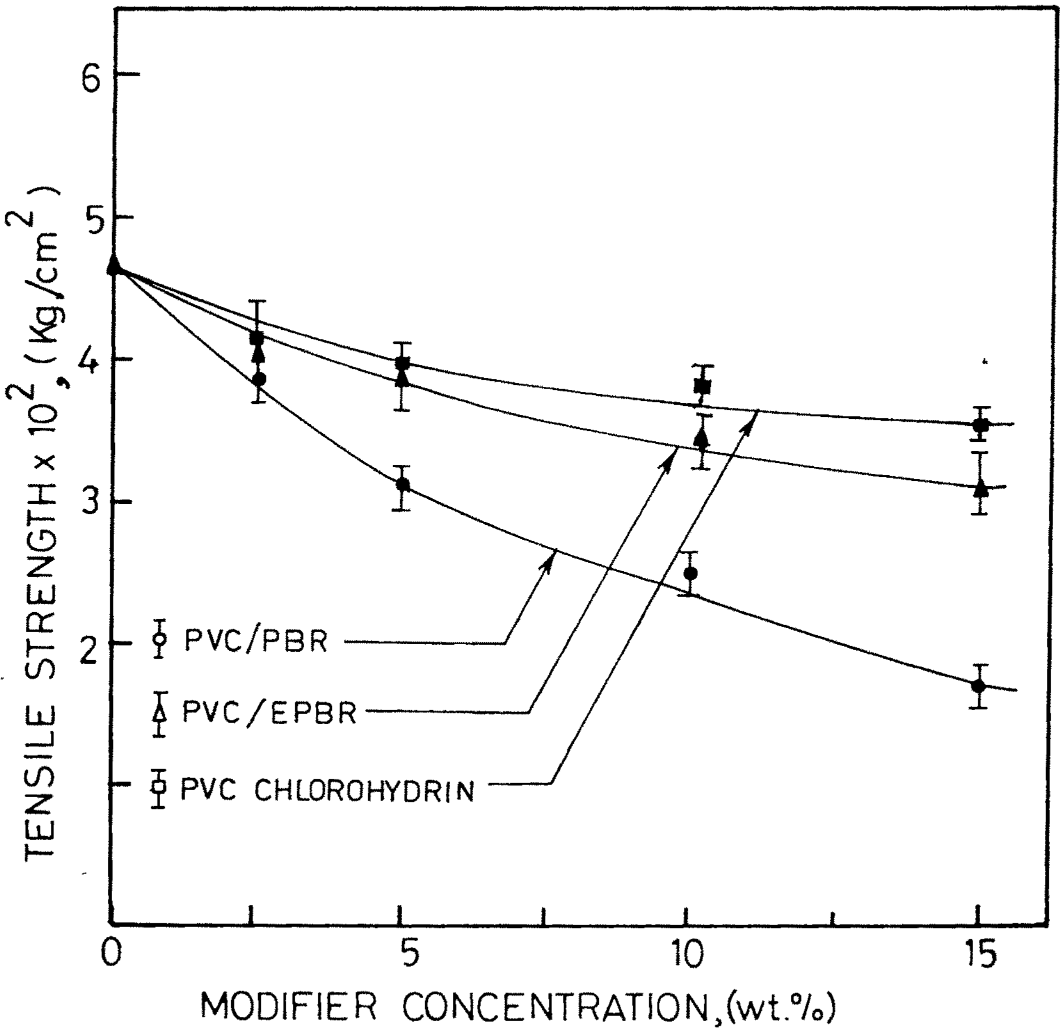


FIG.3.26.INFLUENCE OF DIFFERENT MODIFIERS AND THEIR CONCENTRATIONS ON TENSILE STRENGTH OF PVC AND ITS BLENDS.

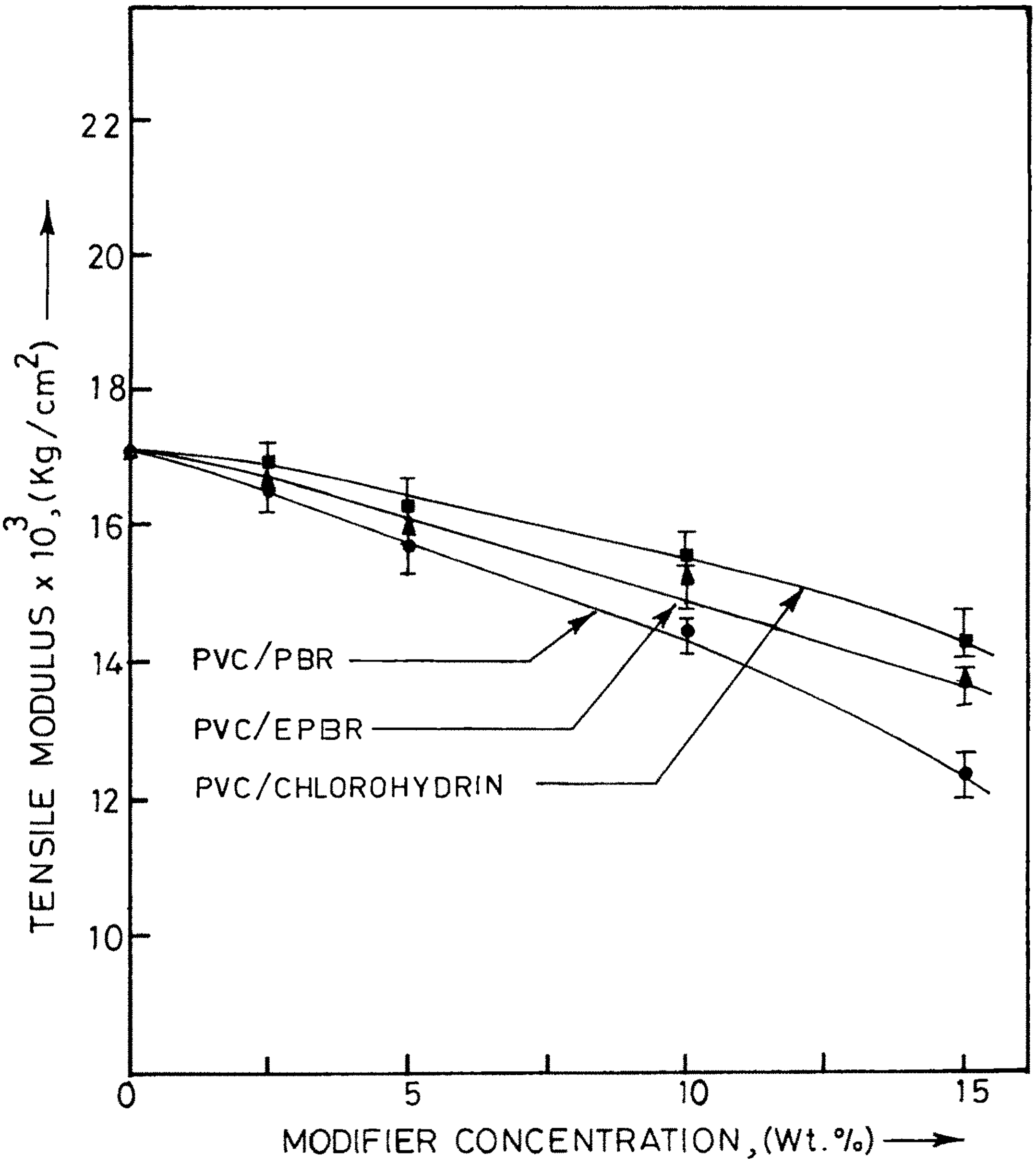


FIG 3.27. INFLUENCE OF DIFFERENT MODIFIERS AND THEIR CONCENTRATIONS ON TENSILE MODULUS OF PVC AND ITS BLENDS.

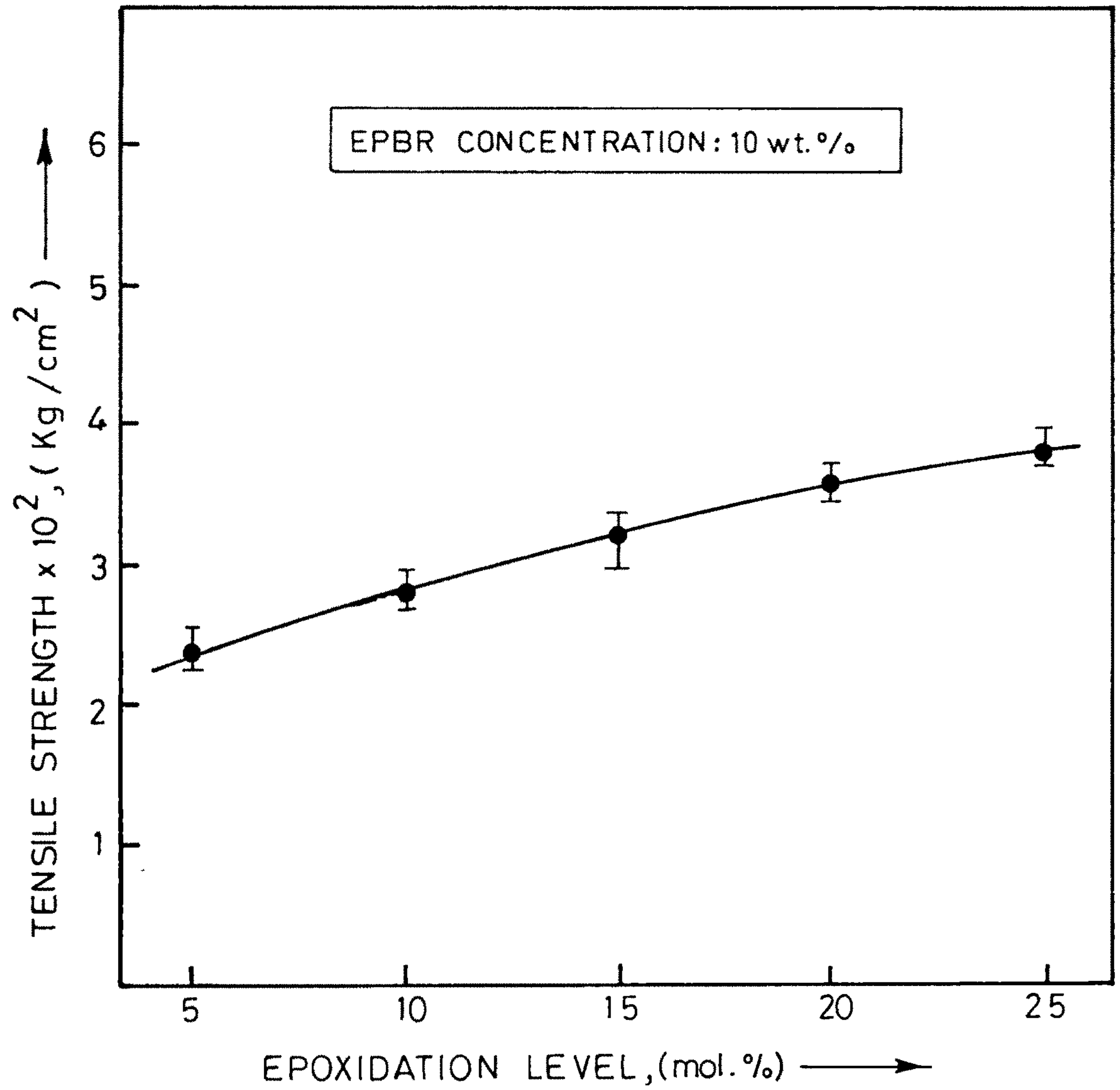


FIG.3.28. INFLUENCE OF EPOXIDATION LEVEL OF EPBR ON TENSILE STRENGTH OF PVC BLENDS

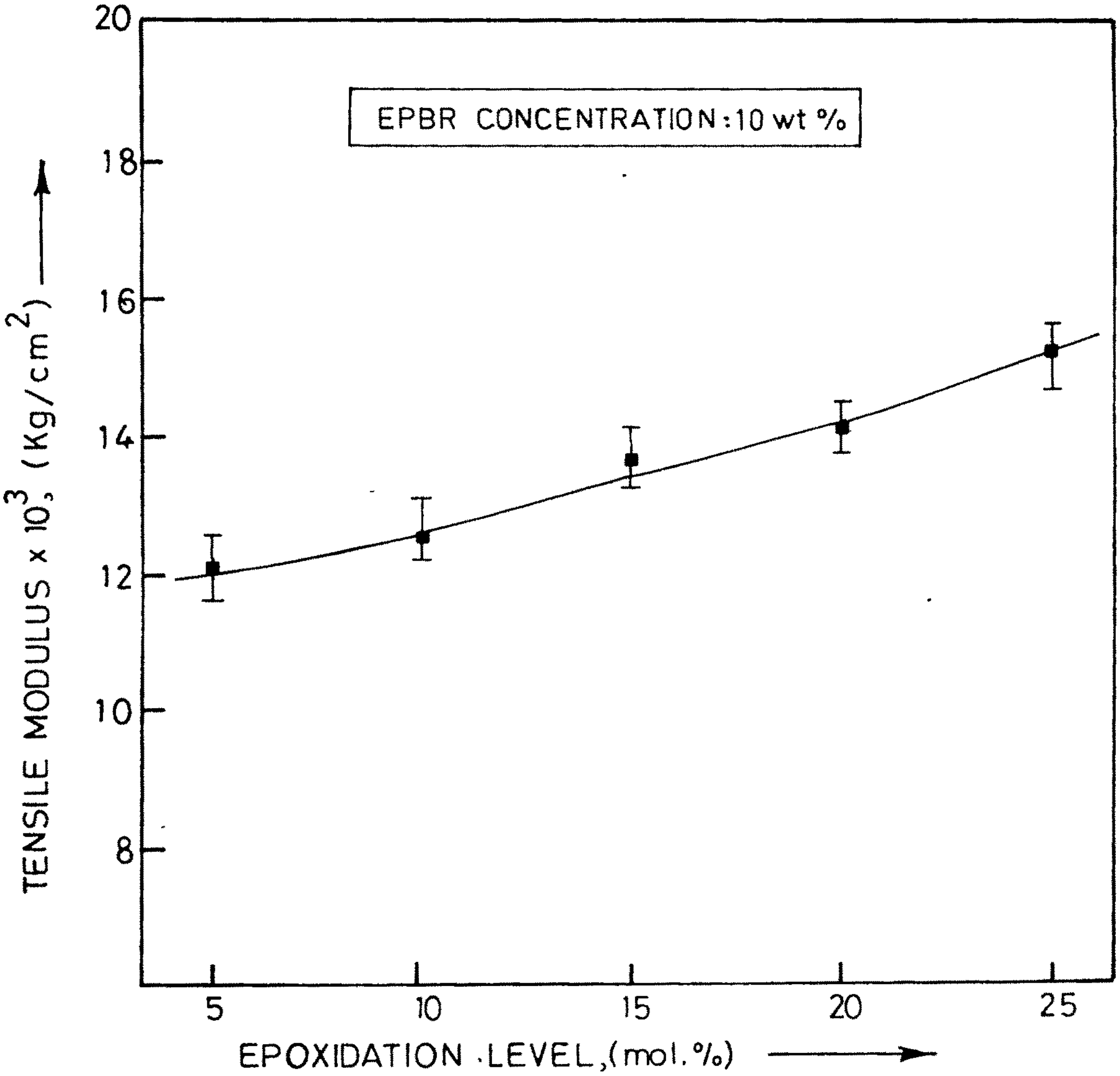


FIG3.29. INFLUENCE OF EPOXIDATION LEVEL OF EPBR ON TENSILE MODULUS OF PVC BLENDS

As expected, both the tensile strength and the modulus of PVC blends are found to decrease with the increase in concentration of the modifiers. This may be due to the plasticization effect caused by the modifiers. However, the extent of reduction in tensile strength and modulus depends on the nature of the rubbery phase. This may be explained on the basis of relative compatibilities of the components with PVC. The polar nature of modified PBR induces a certain degree of compatibility with PVC by strong interaction which is reflected in the relatively better porperties of their blends with PVC.

3.3.5.2 Flexural properties

The flexural strength and flexural modulus of PVC blends with PBR, EPBR and chlorohydrin in different concentrations are depicted in (Fig. 3.30, 3.31). The flexural strength gradually decreases with the increasing incorporation of all the modifiers. In the case of PVC/PBR blends the reduction of flexural strength is maximum and in the case of PVC/ chlorohydrin it is minimum. Again PVC/EPBR shows an intermediate loss in its flexural strength. Flexural modulus of the above blends shows the similar behaviour.

The flexural strengths of PVC blends with 10 wt% EPBR of different epoxidation levels are shown in (Fig. 3.32). Here the flexural strength increases significantly from 10 mol% of epoxidation level with a tendency to level off above 20 mol%. The flexural modulus of PVC blends with 10 wt% EPBR of different epoxidation levels are shown in (Fig. 3.34). Here

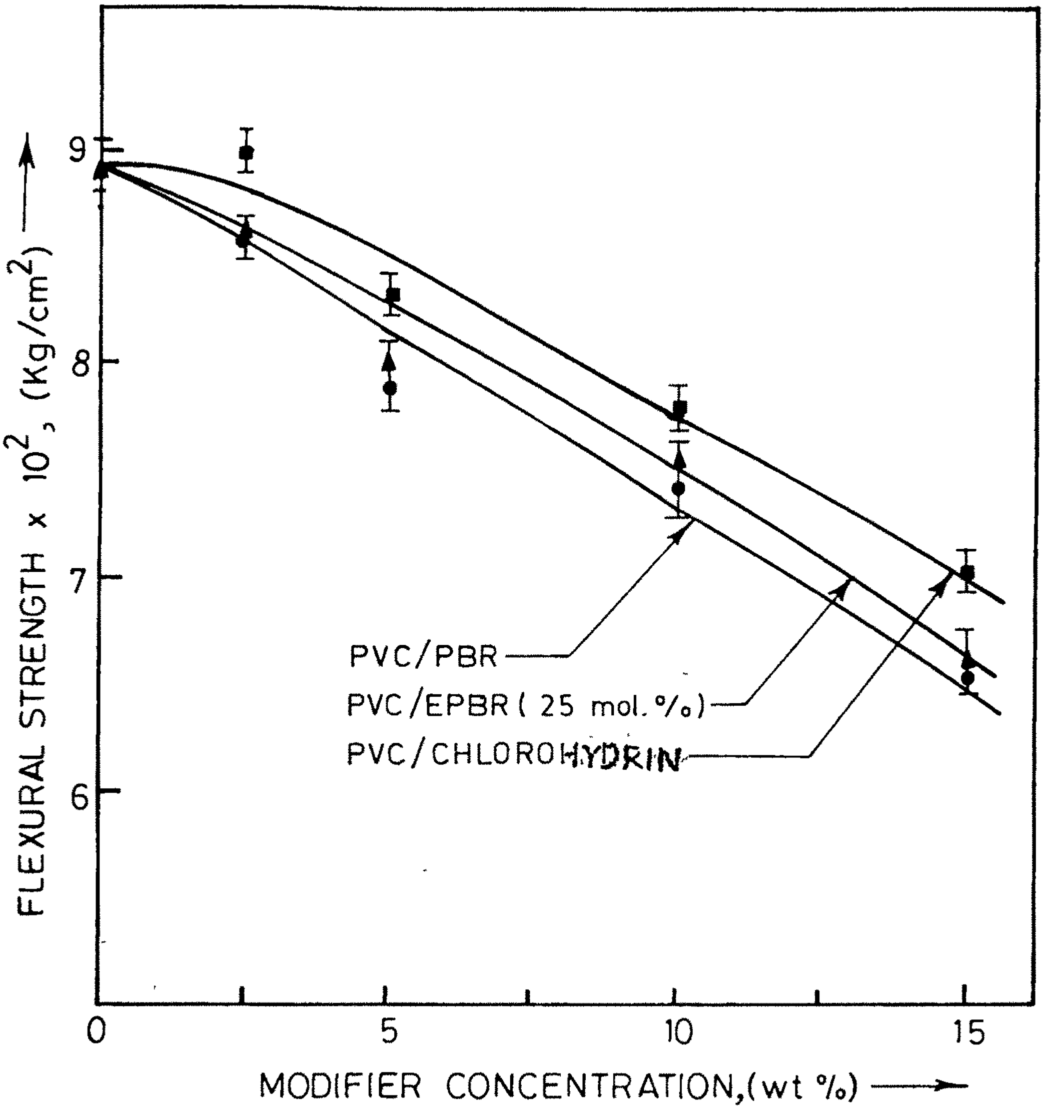


FIG3.30. INFLUENCE OF VARIOUS MODIFIERS OF DIFFERENT CONCENTRATIONS ON THE FLEXURAL STRENGTH OF PVC AND ITS BLENDS.

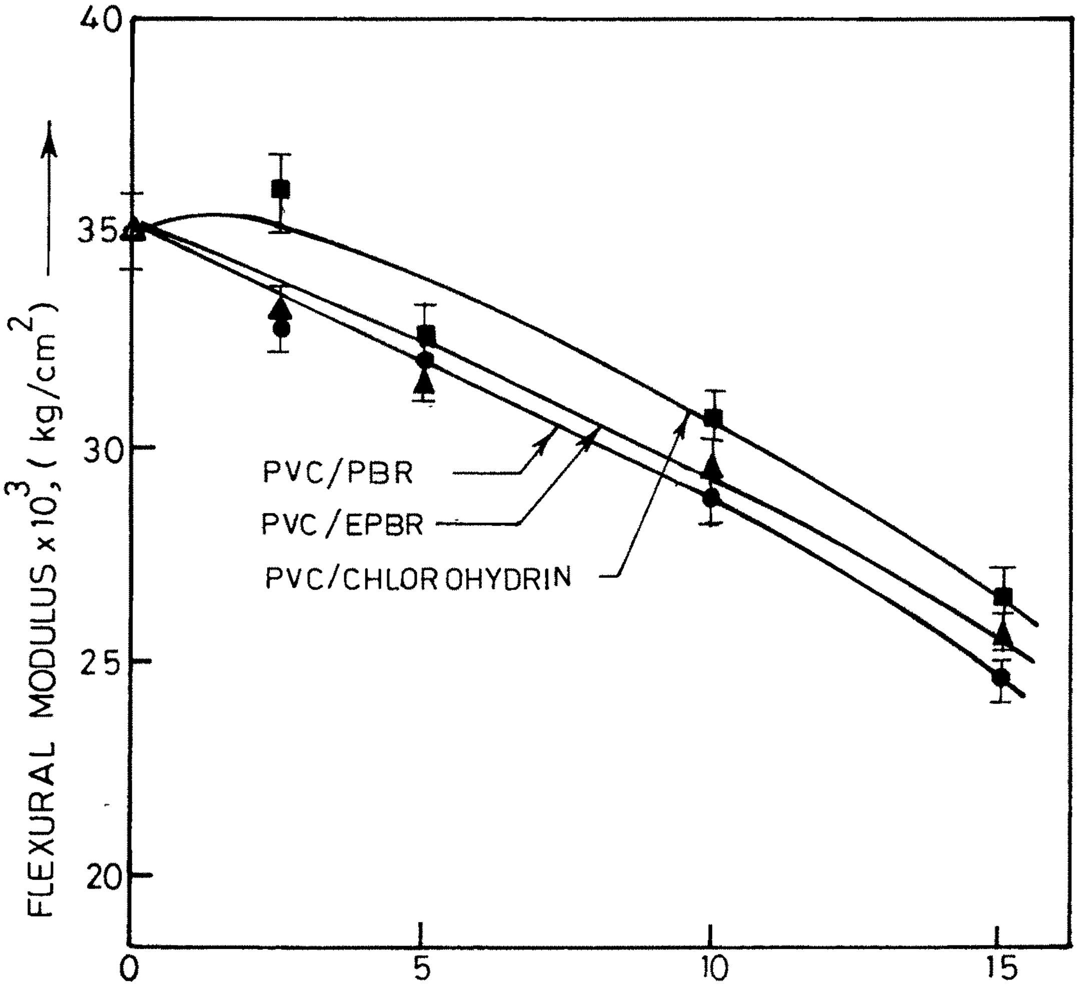


FIG 3.31. INFLUENCE OF DIFFERENT MODIFIERS AND THEIR CONCENTRATIONS ON FLEXURAL MODULUS OF PVC AND ITS BLENDS

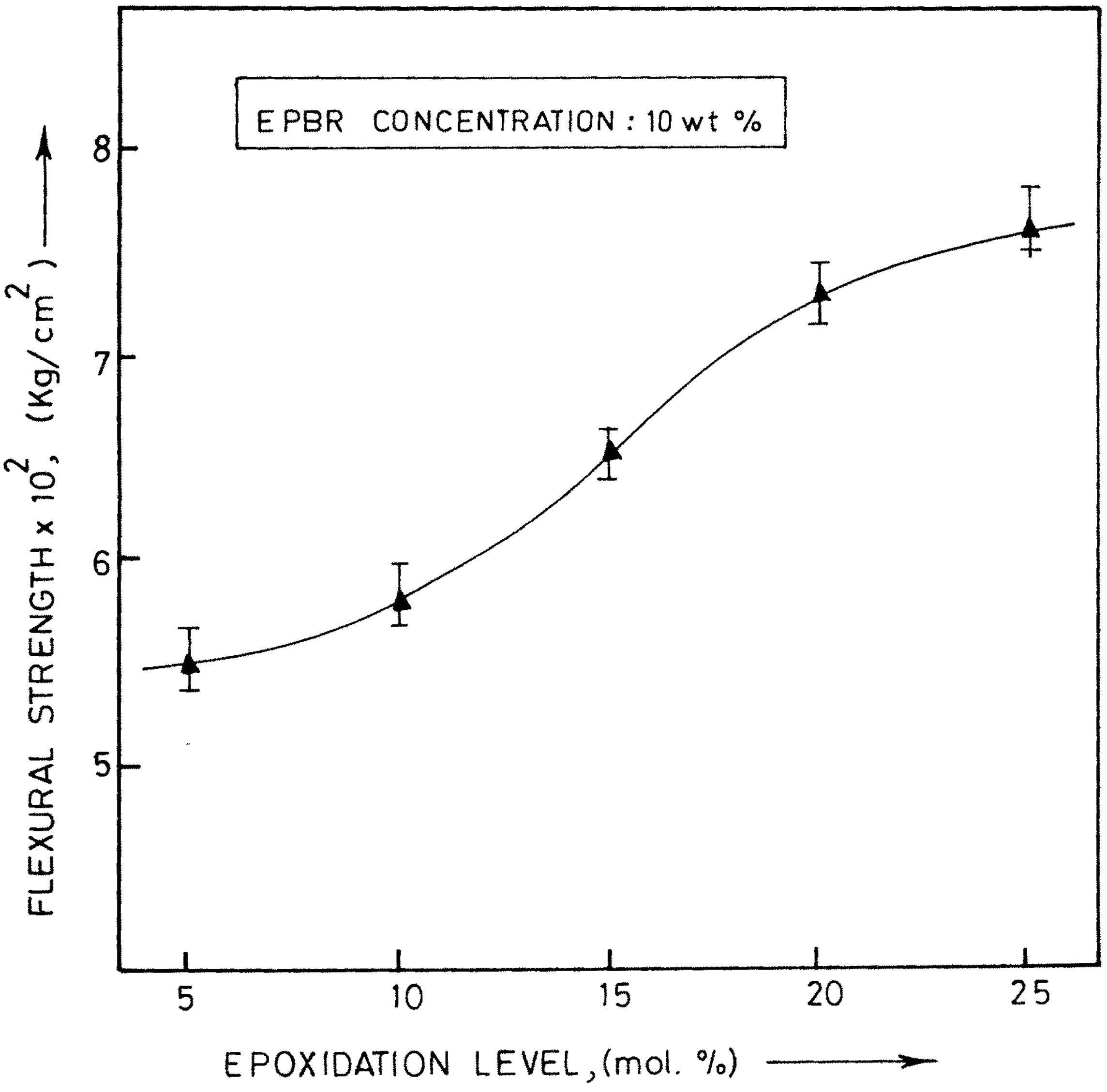


FIG3.32. INFLUENCE OF EPOXIDATION LEVEL OF EPBR ON THE FLEXURAL STRENGTH OF PVC BLENDS

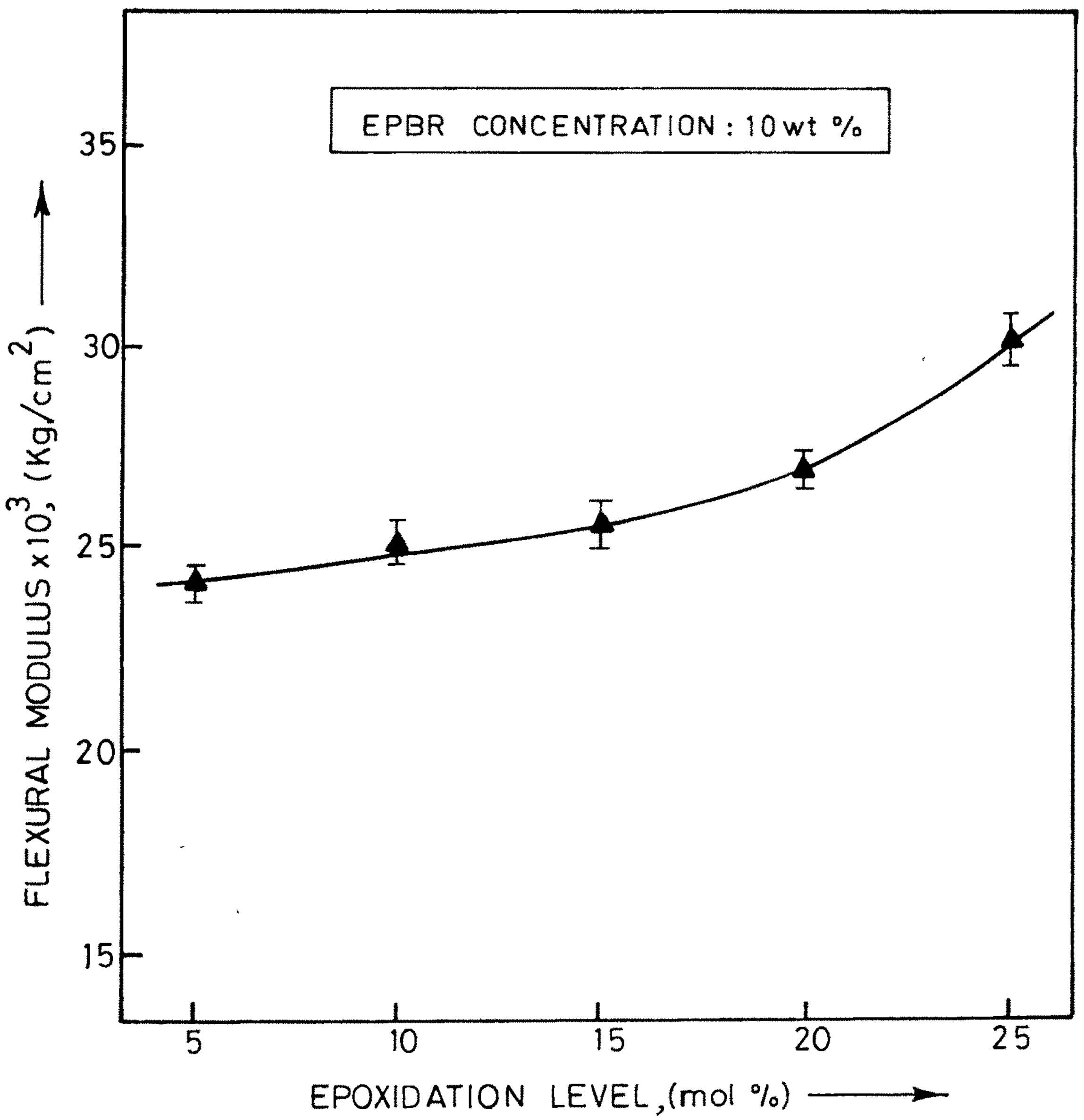


FIG.3.33. INFLUENCE OF EPOXIDATION LEVEL OF EPBR ON FLEXURAL MODULUS OF PVC BLENDS

again the flexural modulus increases with increasing epoxidation level and the blends with 25 mol% exhibits maximum flexural modulus.

Like the tensile properties, the flexural strength and the flexural modulus can also be explained on the basis of relative compatibility of various modifiers with PVC. The concept of additive behaviour of tensile and flexural properties is used as an indication of the compatibility of components in the blends .

3.3.5.3 Impact strength

The Izod impact strength values (notched) of PVC blends with PBR, EPBR and chlorohydrin are presented in (Fig. 3.34). PVC/PBR blends show a gradual decrease in their impact strength with increased PBR content upto 15 wt%. On the other hand, blends containing 10 wt% of EPBR as well as chlorohydrin show a significant rise in the Izod impact strength. However, with further increase in the concentration of either EPBR or chlorohydrin, impact strength again decreases. Among all the three modifiers, it can be easily observed that chlorohydrin provides maximum impact strength closely followed by EPBR, while PBR leads to deterioration in impact strength.

Figure 3.35 shows the impact strength of PVC/EPBR blends (90:10) in which EPBR of various epoxidation levels were used (b_1, b_2, b_3, b_4, b_5). These results show that impact strength increases with increasing of epoxidation level of the modifier.

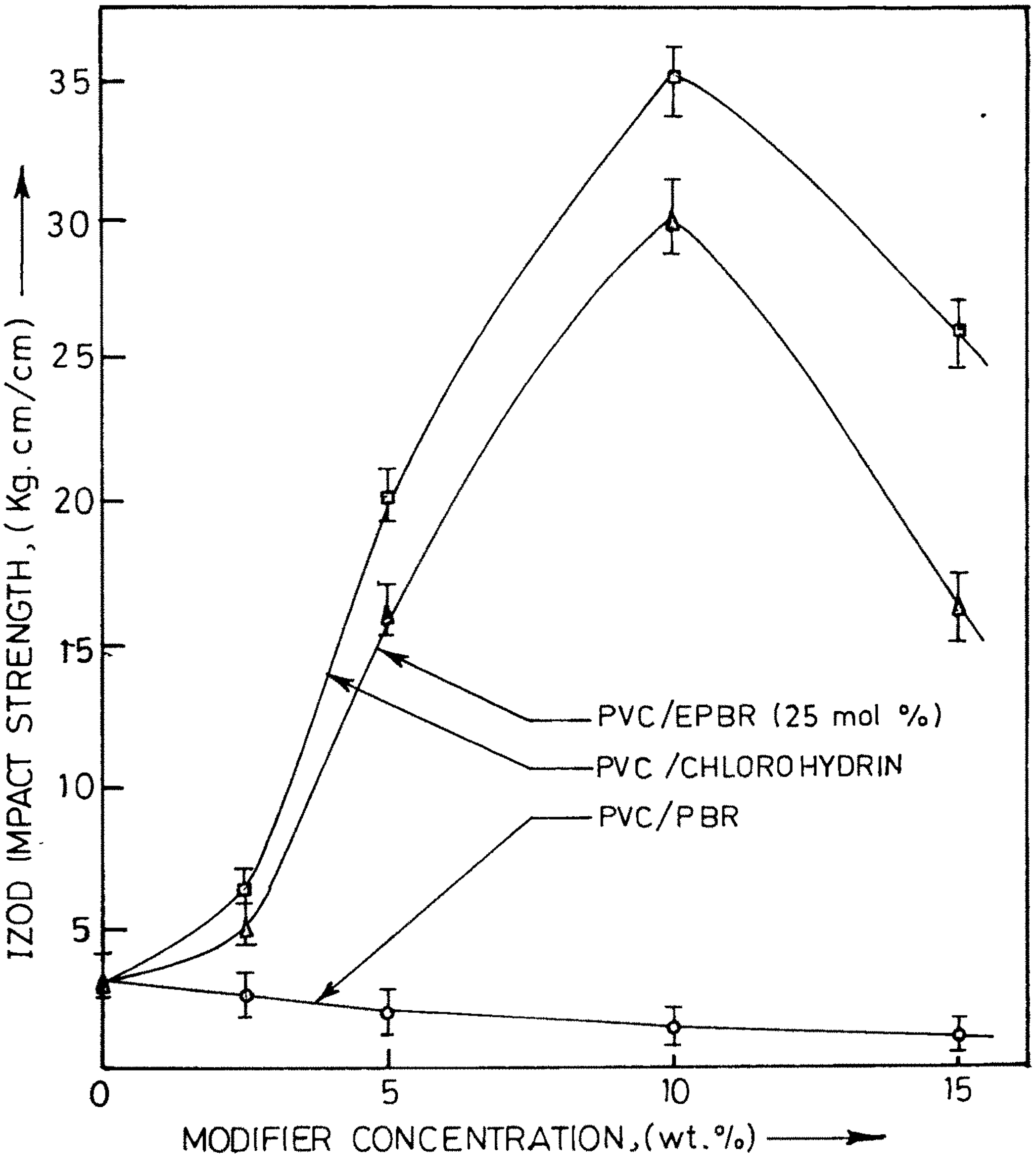


FIG. 3.34. INFLUENCE OF DIFFERENT MODIFIERS AND THEIR CONCENTRATIONS ON IZOD IMPACT STRENGTH OF PVC AND ITS BLENDS

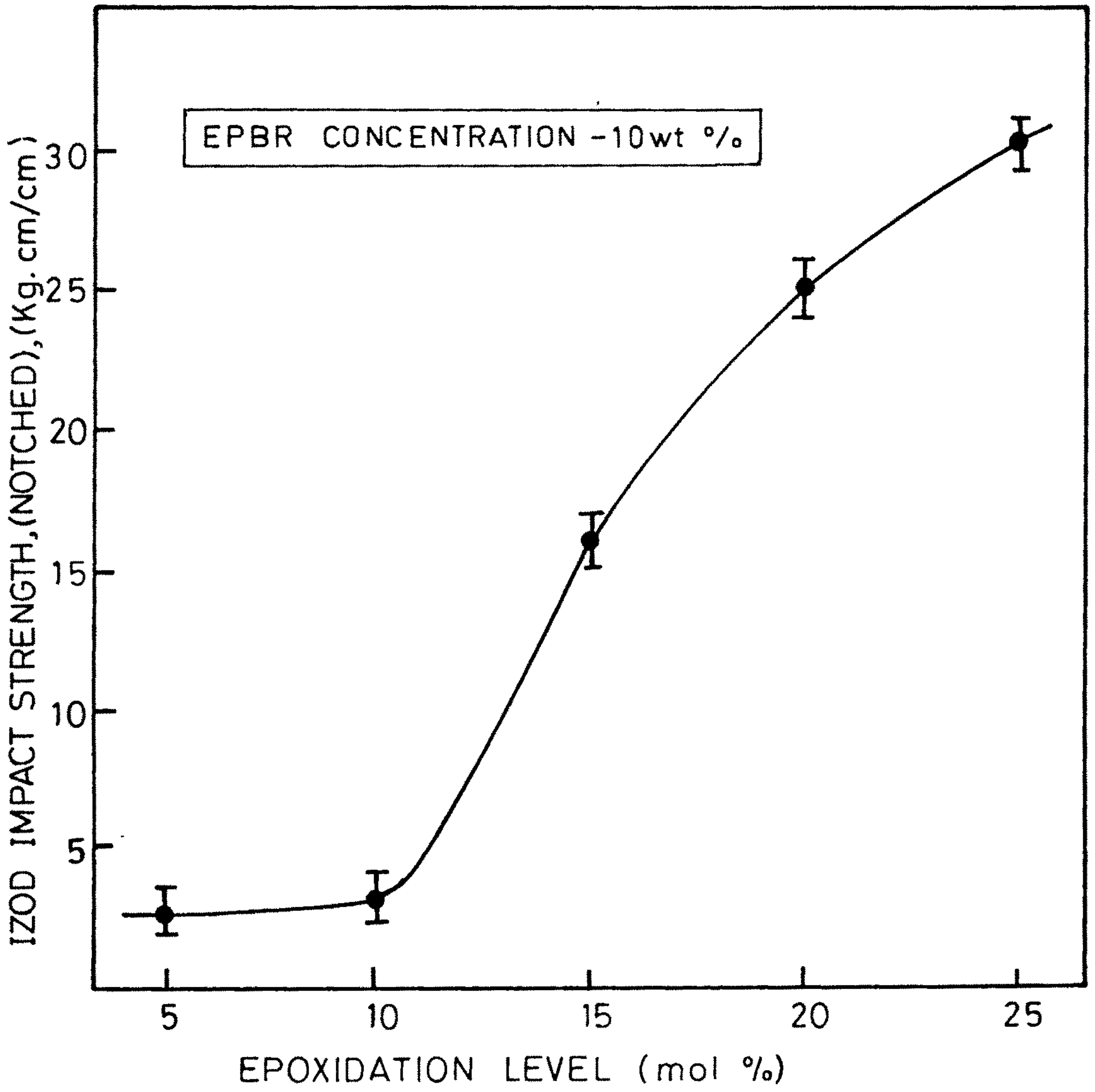


FIG.3.35 INFLUENCE OF EPOXIDATION LEVEL OF EPBR ON IZOD IMPACT STRENGTH OF PVC BLENDS.

It has generally been seen that, ~~the~~ optim~~um~~al dispersion and adhesion of the rubbery phase with PVC are the basic requirements of impact modification[25,26]. The word "Optimum" signifies sufficient compatibility, i.e., neither total miscibility nor complete immisicibility between the components. Thus the behaviour of the present blends 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 incorporation of polarity on to PBR is expected to facilitate ← stronger interaction between chemically modified polar rubber (EPBR, chlorohydrin) with polar PVC. Thus, surface adhesion would be preferred. An optimum dispersion and adhesion of EPBR in PVC and chlorohydrin in the PVC matrix is therefore expected. However, due to its nonpolar nature, PBR does not have such an interaction. ~~hence~~ Thus leads to poor impact strength. Similarly, PVC/EPBR blends with lower epoxidation levels (b_1, b_2, b_3) do not show much improvement in impact strength. ×

Speculation?

In PVC/EPBR blends, micro level interaction may cause a drastic reduction of average dimensions of the dispersed phase particles which leads to improvement in impact strength. However, particle size measurements could not be done due to experimental limitations. Among the blends studied, PVC/EPBR(c_3) and PVC/chlorohydrin(d_3) blends are found to show the best impact strength.

What limitations?

3.3.5.4 Dynamic Mechanical Analysis

Important information concerning relaxation transitions occurring on a molecular scale can be ~~derived~~ acquired by subjecting polymers to small amplitude cyclic deformations. Data obtained over a broad temperature range allow us to understand how one polymer can modify the dynamic properties of another component in the blend and ultimately aid in the design of polymer blends with desirable physical properties[27,28]. The present experimental study ~~examines~~ considered the influence of different impact modifiers and their concentration on the dynamic mechanical behaviour (tan δ curves) of PVC blends. A qualitative measure of interactions between the components of a blend may be obtained from the study of Tg of the blends.

The glass transition temperature of PVC, PBR EPBR (25 mol%) and PbR chlorohydrin are 88°C, -100°C, -80°C and -76°C respectively. Tg the values of PVC and the modifiers are wide apart, the former is plastic and the latter is elastomeric in nature. Tan δ curves of PVC and its blends obtained from the DMA experiments are given in (Fig. 3.36 and 3.37). Such plots afford the determination of Tg of the polymer samples. It is evident from these figures that PBR and EPBR with the lower degree of epoxidation do not alter the Tg of PVC, which indicates that these modifiers have little or no compatibility with PVC. On the other hand, PVC/EPBR blends with higher epoxidation level and PVC/chlorohydrin blends exhibit slightly lower Tg than that of PVC (also the peaks are broader). These suggest a certain degree of compatibility between PVC and the modifiers. More

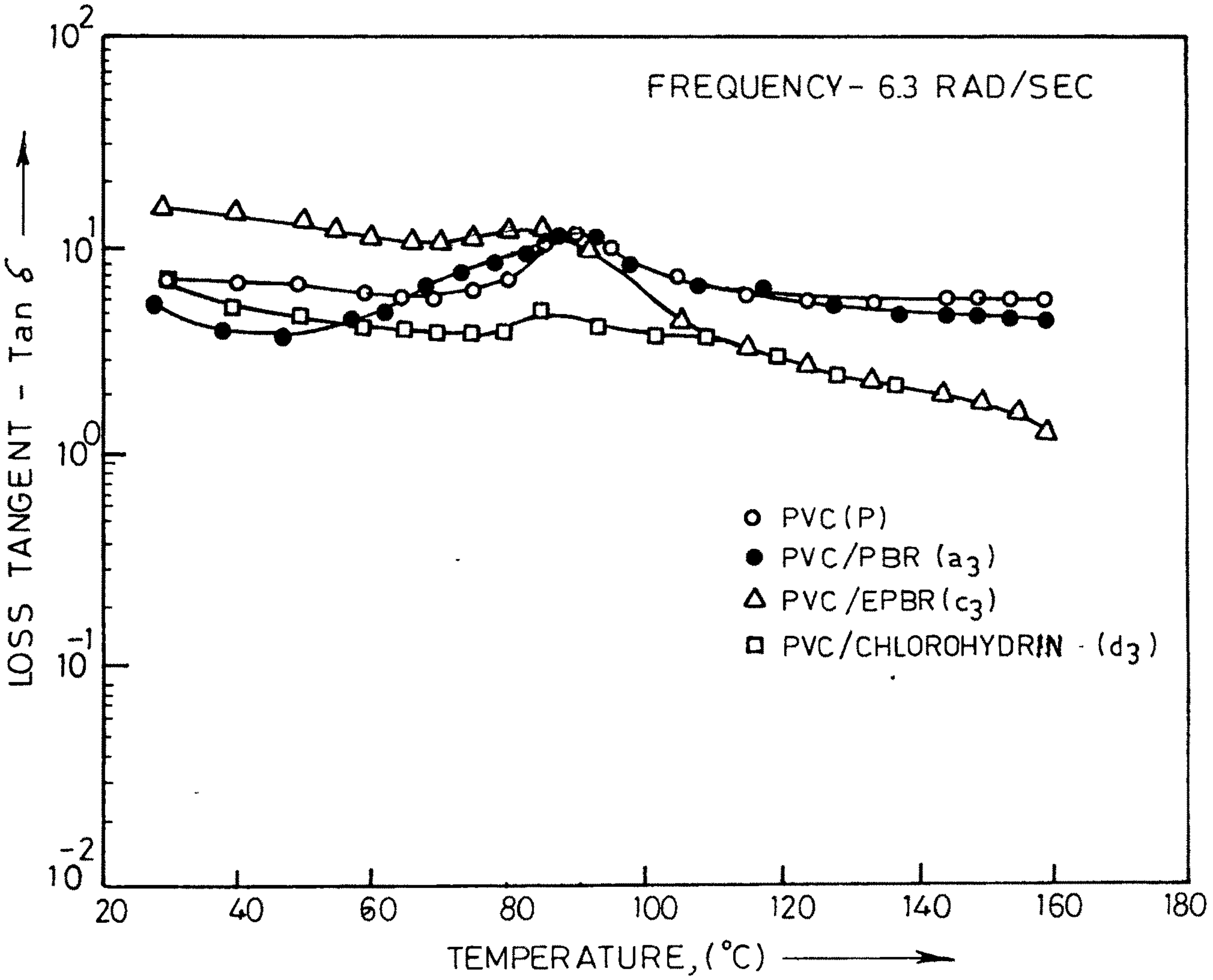


FIG 3 36. DYNAMIC MECHANICAL BEHAVIOUR (Tan δ curves) OF PVC AND ITS BLENDS WITH DIFFERENT MODIFIERS

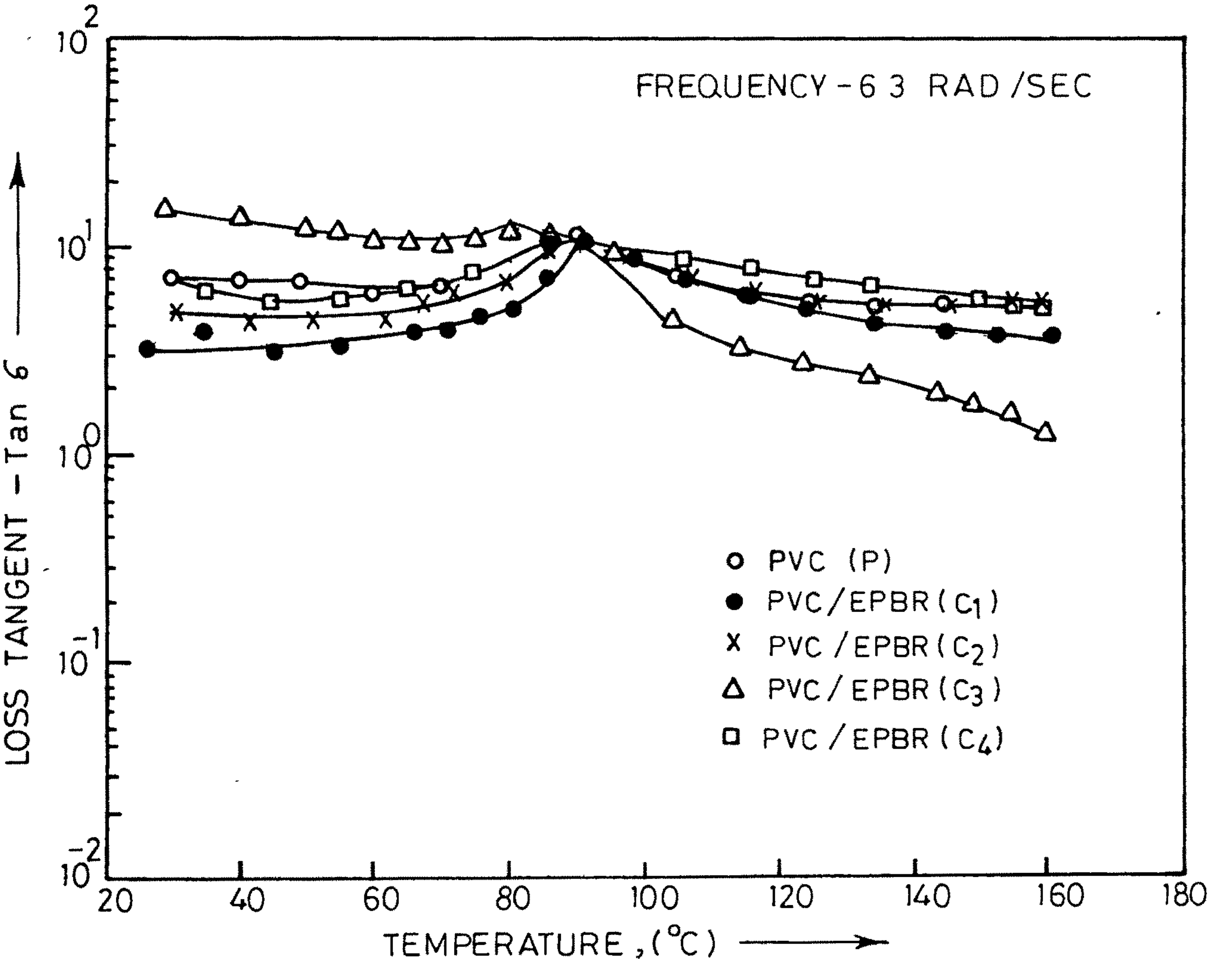


FIG.3.37. DYNAMIC MECHANICAL BEHAVIOUR (Tanδ curves) OF PVC AND PVC/EPBR BLENDS.

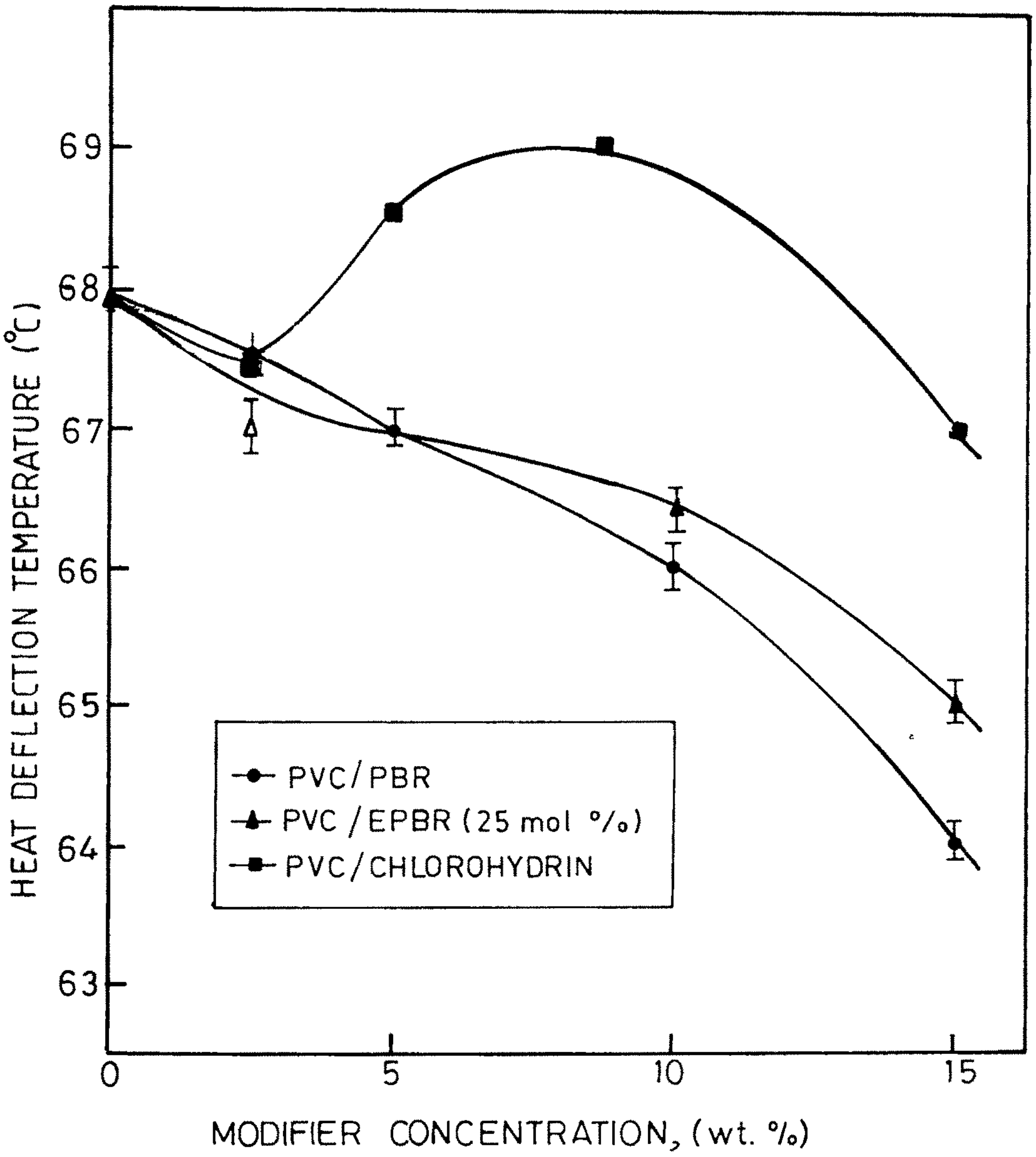


FIG 3.38. INFLUENCE OF DIFFERENT MODIFIERS AND THEIR CONCENTRATIONS ON HEAT DEFLECTION TEMPERATURE OF PVC AND ITS BLENDS

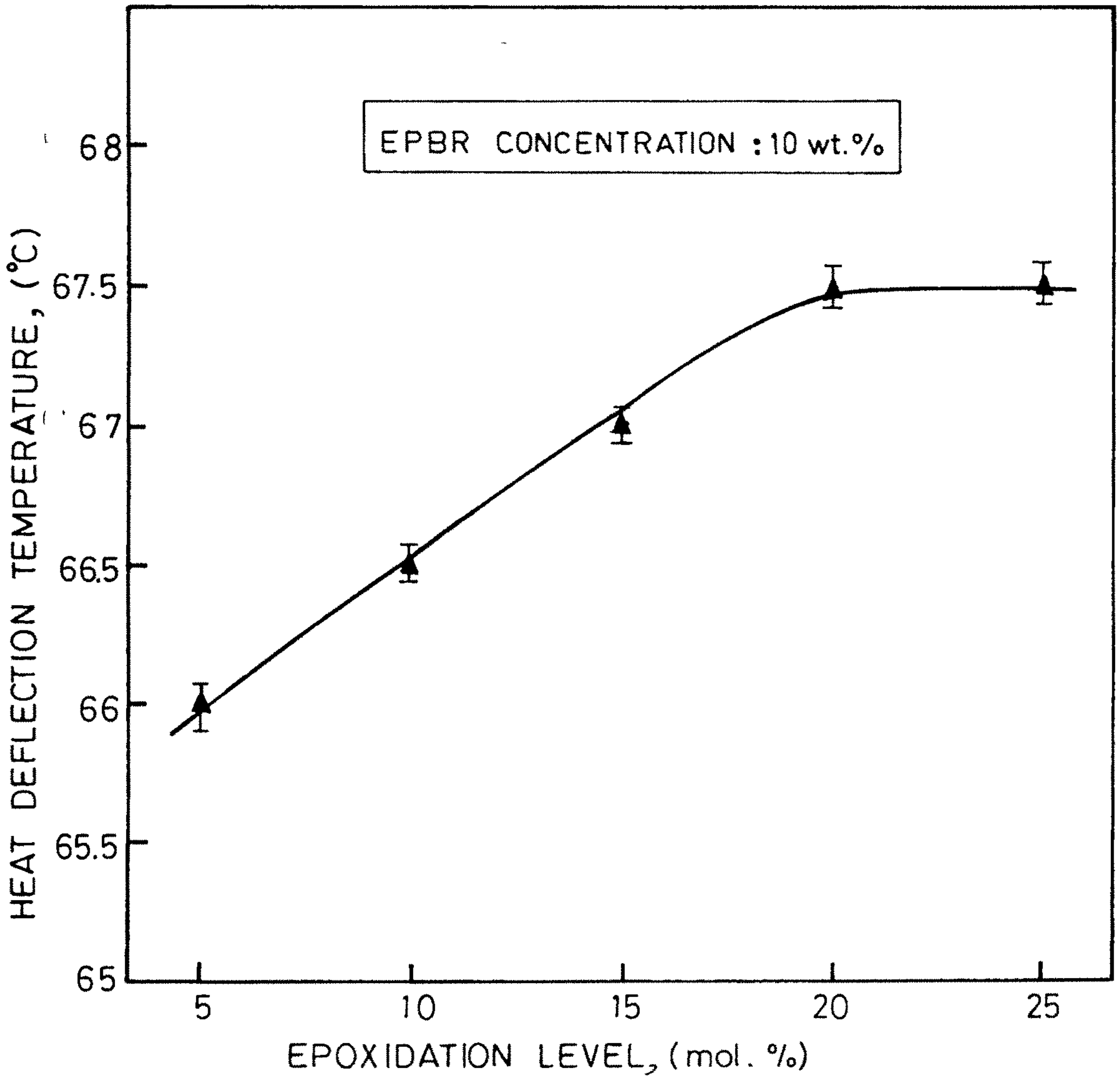


FIG 3.39 INFLUENCE OF EPOXIDATION LEVEL OF EPBR ON HDT OF PVC BLENDS

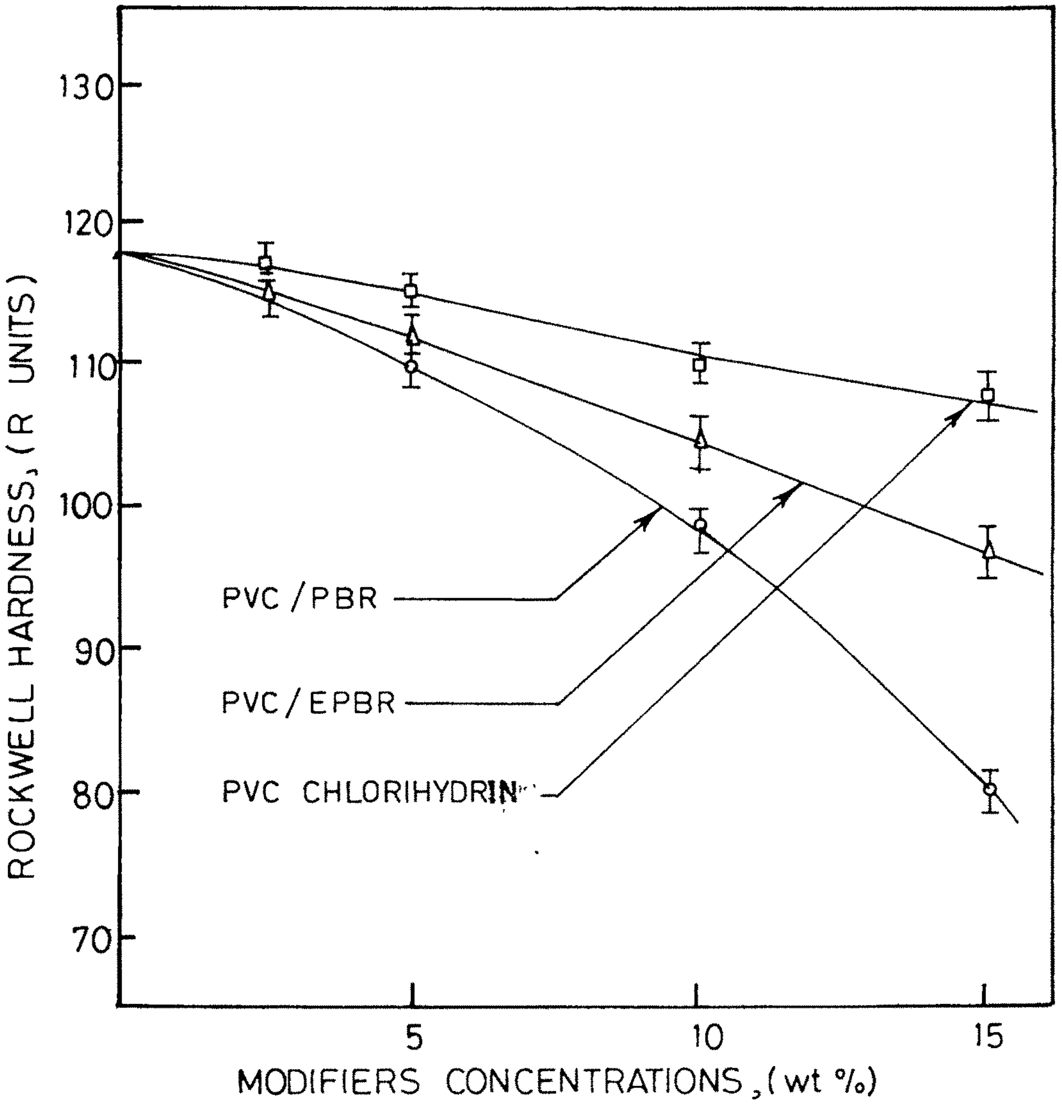


FIG. 3.40 INFLUENCE OF DIFFERENT MODIFERS AND THEIR CONCENTRATIONS ON ROCKWELL HARDNESS OF PVC AND ITS BLENDS.

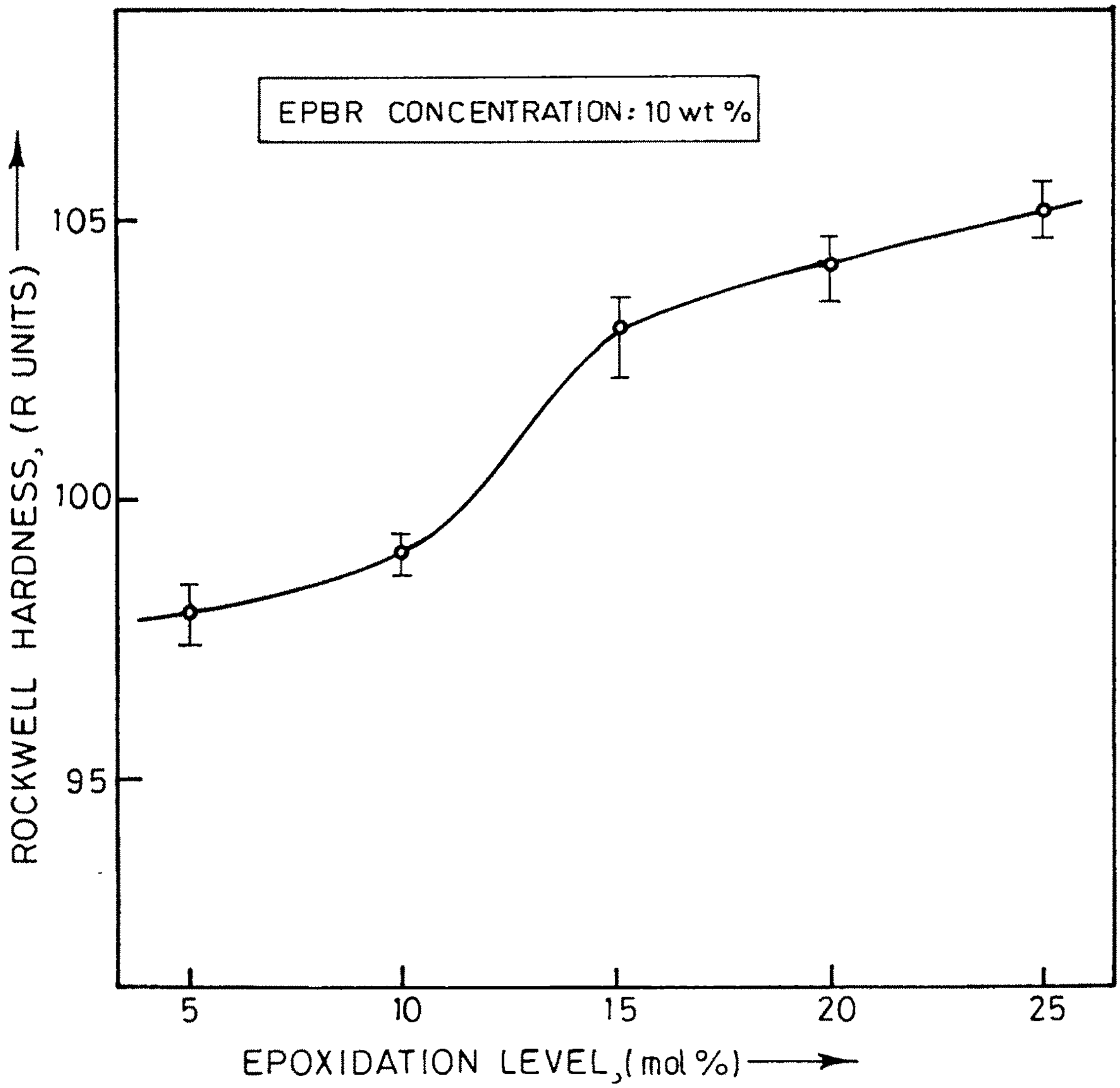


FIG.3.41. INFLUENCE OF EPOXIDATION LEVEL OF EPBR ON ROCKWELL HARDNESS OF PVC BLENDS

information regarding this aspect could have been gathered from DMA studies at low temperature. However, due to experimental limitations such a study was not carried out.

3.3.5.5 Heat Deflection Temperature (HDT)

Heat Deflection Temperature is another important property of polymeric materials. It can be considered as the upper temperature limit upto which the material can support the load to any appreciable time. It indicates the continuous working temperature of the material. The HDT values of PVC and the various blends are given in Table 3.7-3.10. The data shows that HDT remains nearly constant with the incorporation of chlorohydrin in PVC. Mixing EPBR (25 mol%) with PVC brings about a marginal decrease of about 1°C at 5 wt% concentration (Fig.3.38). Only, PVC blends with PBR show a fall of 4°C in HDT at 15 wt% concentration. Behaviour of PBR is obvious because it has low tensile strength and flexural modulus. ?

?

PVC/EPBR blends show an increase in HDT with increasing epoxidation level (Fig. 3.39). The Higher Tg and better compatibility with PVC at higher epoxidation may be responsible for such a behaviour. For the same reasons, chlorohydrin incorporation also gives better results.

3.3.5.6 Rockwell hardness

Figure 3.40 shows variation of Rockwell hardness of PVC and its blends with different concentrations of modifiers. Figure 3.41 presents the influence of epoxidation level on the Rockwell hardness of PVC/EPBR blends. Rockwell hardness values for all the blends are given in Table 3.7-3.10. From the Tables it can be inferred that all the blends have lower Rockwell hardness values than that of neat PVC. Obviously, this is due to the presence of soft rubber of very low Rockwell hardness in the blend systems. In all the blends, hardness values decrease as modifier concentration increases. In PVC/PBR blends, Rockwell hardness values decrease more steeply with increasing PBR concentration. In PVC/EPBR blends (b_1, b_2, b_3, b_4, b_5) as epoxidation level increases, Rockwell hardness values increase. PVC/EPBR blends with different compositions (c_1, c_2, c_3, c_4) show that as EPBR concentration increases hardness decreases. However, the reduction in hardness is less in comparison to that of PVC/PBR blends, in all compositions. This may be attributed to some compatibility brought about by epoxidation and the observed ring opening reaction involving these groups. For the same reasons, PVC/chlorohydrin blends show the least reduction in hardness values among the three modifiers used. In other words, PVC/chlorohydrin blends in all compositions show slightly higher Rockwell hardness values compared to the corresponding blends of EPBR, which in turn show higher values than PBR blends.

3.4 Conclusions

Incorporation of high molecular weight PBR into PVC matrix, deteriorates the mechanical properties of the latter. Decreasing trends in tensile and flexural properties, heat deflection temperature (HDT), and Rockwell hardness with increasing concentration of PBR in the blend is a consequence of low glass transition temperature of the rubbery phase. Poorer impact strength of the blends relative to that of PVC may be ascribed to the poor adhesion between the polar PVC and nonpolar PBR This can be easily gleaned from scanning electron micrographs of the impact fractured surfaces of the blends which resemble the brittle fracture observed in the case of neat PVC.

Some interaction between the two phases cannot be ruled out in the melt mixed blends. This is because a small amount of HCl liberated due to PVC degradation has a tendency to undergo addition reaction across the double bonds of PBR, thus bringing about some similarity between the two phases. Removal of HCl prevents autocatalysis of the degradation reaction. For this reason, PBR incorporation leads to improvement in thermal stability of PVC.

Partial epoxidation of PBR introduces polarity into the polymer backbone and hence better interaction with PVC depending on the epoxidation level. This is reflected in the properties of the blends of PVC containing 2.5 to 15 wt% of EPBR (25 mol% epoxy content). Tensile and flexural properties, HDT and Rockwell hardness of these blends, although inferior to that of PVC, are better than those of the corresponding PVC/PBR blends. But the impact strength of PVC improves significantly on EPBR incorporation with a maximum around 10 weight% EPBR; obviously due to a certain degree of compatibility of both the components. The molecular origin of this could be traced to the polar-polar and/or donor-acceptor interaction among the α-hydrogen of PVC and the oxirane group. Further, the HCl liberated due to slight degradation PVC, apart from addition across the double bonds, takes part in ring opening reaction with the oxirane group to generate a small amount of chlorohydrin in situ. This is confirmed by the similarity in infra red spectra of PVC/EPBR blends and that of a blend prepared by mixing PVC. At higher concentration of EPBR, impact strength decreases which shows that phase segregation slowly sets in. The PVC/chlorohydrin blends show higher impact strength than even the PVC/EPBR blends at any given concentration level.

A slow transformation from fragile fracture to ductile fracture can be seen from SEM studies of the PVC/EPBR blends.

EPBR incorporation improves the thermal stability of PVC to a greater extent than that observed with PBR incorporation, which may be related to more efficient absorption of HCl by EPBR than PBR. As mentioned earlier removal of HCl prevents autocatalysis of the degradation process. PVC/Chlorohydrin blends do not show any improvement in thermal stability because most of the epoxy groups are already used up prior to blending.

At a fixed composition (90/10) of PVC/EPBR blends, the higher the degree of epoxidation, higher are the thermal stability and impact strength in the epoxidation range studied. Both the properties tend to level off at higher epoxidation level.

Therefore, partially epoxidized high molecular weight PBR can be effectively used as a property modifier leading to significant gain in impact strength and thermal stability without much loss in other useful properties of PVC. Some improvement in processibility is also an added advantage. Chlorohydrin derivative of PBR can also be used to improve impact strength but it does not contribute much towards thermal stability of PVC.