Studies on Miscibility of Poly(vinyl chloride) with Natural Rubber-*graft*-Polyacrylonitrile and Natural Rubber-*graft*-Poly(methyl methacrylate)

F. E. OKIEIMEN* and I. N. URHOGHIDE

University of Benin, Department of Chemistry, Benin City, Nigeria

SYNOPSIS

The miscibility of poly(vinyl chloride)/natural rubber-*graft*-polyacrylonitrile (PVC/NRPACN) and PVC/NR-*graft*-poly(methyl methacrylate) (PMMA) were studied by differential scanning calorimetry (DSC) and viscometry. DSC curves of PVC/NR graft copolymer blends showed a major endotherm at about 265°C that was assigned to the thermal decomposition of PVC. PVC/NRPMMA blends showed a minor endothermic peak at about 124°C and the PVC/NRPACN blends showed a broad peak (which develops into two peaks) at about 160°–180°C, respectively. Absolute viscosity versus weight percent PVC plots of the two sets of blends were nonlinear. X-ray diffraction patterns of the PVC/NRPACN blends showed overlapping spacings due to the constituent polymers. Phase-contrast micrographs of the PVC/NRPACN blends showed gross phase discontinuity. The heats of mixing solutions of PVC blended with NRPMMA were found to be well above the upper limit of miscibility. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Recently, interest in the synthesis and use of high molecular weight plasticizers for poly(vinyl chloride) (PVC) has increased. This is due to such advantages as low volatility and extractibility as well as low migration level compared to low molecular weight plasticizers. Margaritis and Kalfoglous[1,2] and Varughese and De[3] showed that PVC/ethylene natural rubber (ENR) blends exhibit a single phase transition temperature T_g, which lies between that of PVC and ENR, thus confirming miscibility at the molecular level. The miscibility of graft copolymers of styrene, acrylonitrile (ACN), and methyl methacrylate (MMA) on EPDM (ethylene-propylene-diene terpolymer) rubbers with PVC was investigated by Falk et al.[4] They found that PVC was miscible with the graft copolymers of styrene, ACN, or MMA with EPDM rubbers.

In our previous study, we examined[5] the miscibility of NR-*graft*-poly(ethyl methacrylate) (NRPEMA) and NR-*graft*-polyacrylonitrile-*co*-poly(methyl methacrylate) (NRPACNPMMA) with PVC and found that NRPACNPMMA formed semimiscible blends with PVC, but NRPEMA/PVC blends were immiscible. In continuation of these studies, this report examines the miscibility of *graft*-PACN and NRPMMA with PVC.

EXPERIMENTAL

Materials

NR obtained from Utagba-uno rubber estate, Nigeria was extracted with acetone for 24 h. ACN and MMA monomers (Aldrich Chemicals) were purified from hydroquinone stabilizer by extraction with aqueous alkaline solution followed by distillation. PVC (MW 200,000) obtained from BDH Ltd. was used without further purification.

Methods

NR (3 g) was dissolved in toluene (250 mL) at 60°C in a 1-L 4-neck round-bottom flask under reflux. ACN (9 mL) was added to the contents of the flask and flushed with nitrogen gas for 1 h before benzoyl
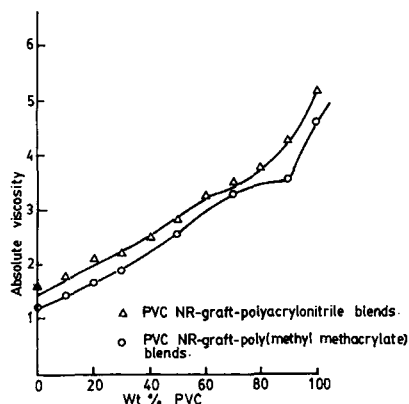
Figure 1 Absolute viscosity vs. composition of various PVC blends at 45°C.

peroxide (1.2 g in 50 mL toluene) was added. The reaction was allowed to proceed for 6 h after which the contents of the flask were poured into 750 mL of 2.5% (w/v) formic acid solution. The coagulum that ensued was washed with several portions of water and dried in a vacuum at 50°C until it gave constant weight. The ungrafted PACN was extracted with dimethyl formamide using a Soxhlet apparatus. The percent graft level, P_g, was taken as the ratio of the weight of PACN added to the weight of the rubber multiplied by 100.

The same procedure was adopted for the synthesis of NRPMMA. MMA (9.8 mL) and benzoyl peroxide (1.0 g) were used. The ungrafted PMMA was extracted with acetone.
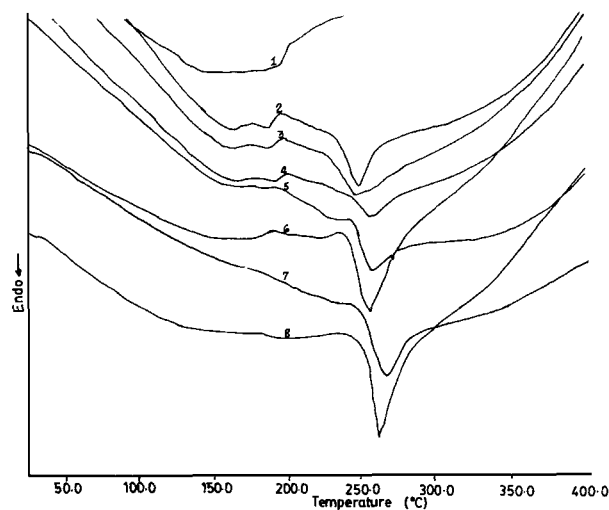

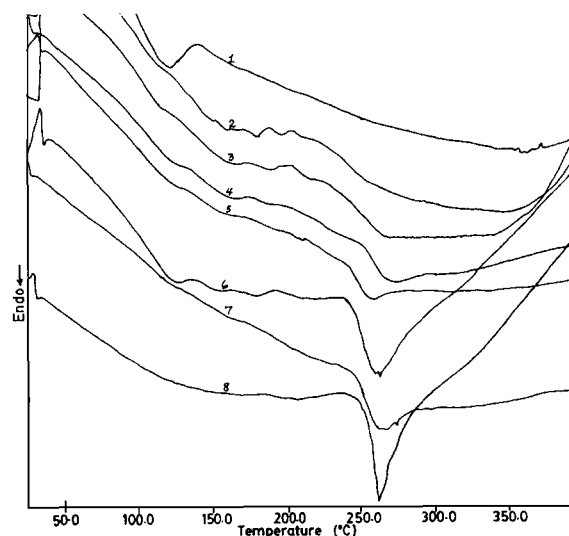**Figure 2** DSC curves of PVC/NRPACN blends. For sample codes 1–8, see Table I.

Figure 3 DSC curves of PVC/NRPMMA blends. For sample codes 1–8, see Table II.

The NRPACN and NRPMMA samples used for blending contained about 38 and 36% of PACN and PMMA, respectively. The blends were made by mixing 2% (w/v) solutions of the polymers in cyclohexanone in the required proportions. The solutions were poured into petri dishes and the solvent evaporated in a stream of air.

Absolute viscosity measurements of the solutions of the polymer blends were measured using an Ubbelohde suspended level viscometer. The viscometer was first calibrated with cyclohexanone.

Differential scanning calorimetry (DSC) measurements of the blends were carried out in a nitrogen atmosphere using a Perkin–Elmer 7 Series Thermal Analysis System. Calibration was made with indium standard. The samples of the polymer blend (between 5 and 7 mg) were sealed in aluminum pans and heated at 10°C/min.

Table I   Sample Codes for PVC/NRPACN Blends

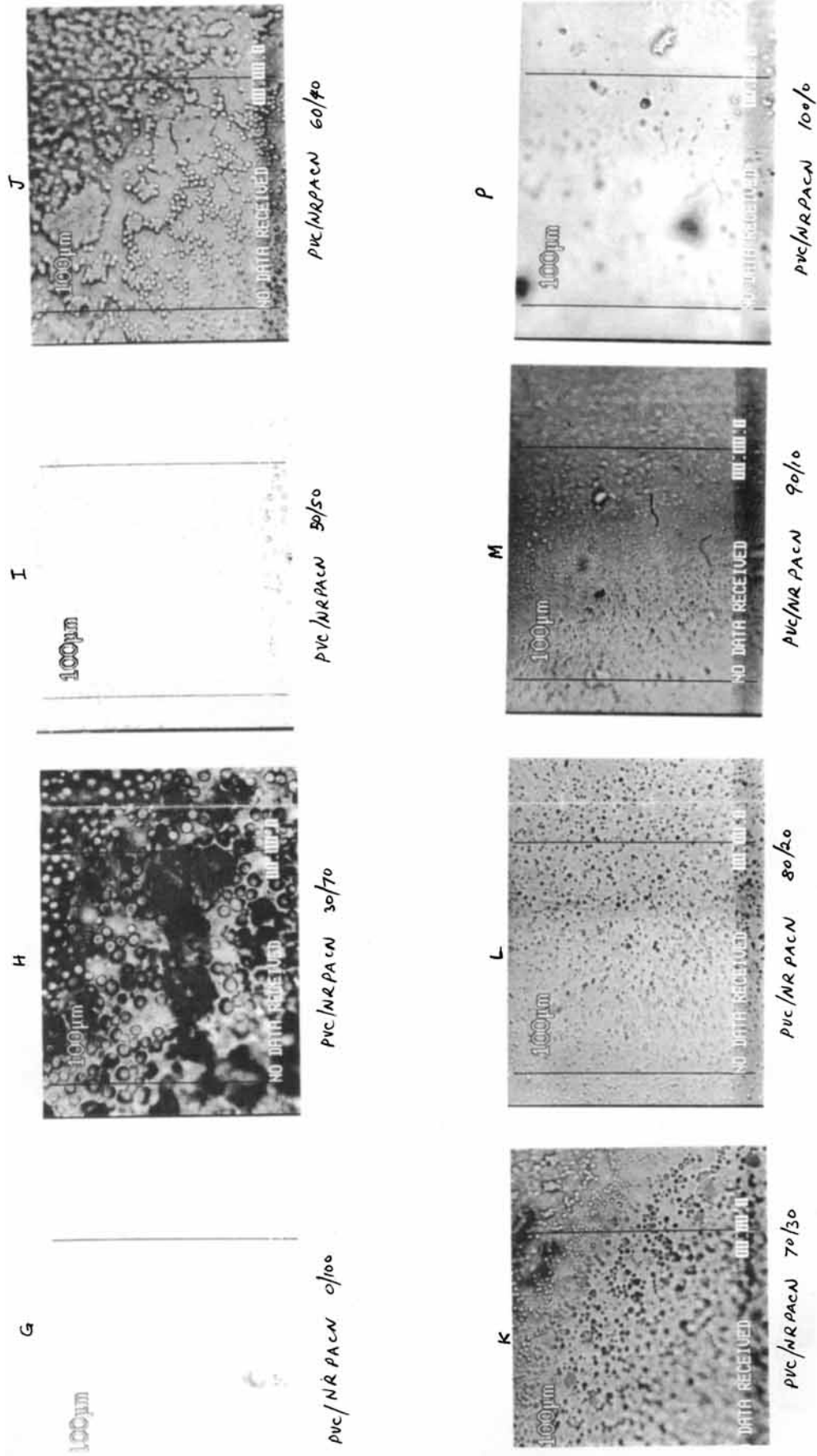| Sample Code	DSC Curve
PVC/NRPACN 0/100	1
PVC/NRPACN 10/90	2
PVC/NRPACN 20/80	3
PVC/NRPACN 30/70	4
PVC/NRPACN 50/50	5
PVC/NRPACN 70/30	6
PVC/NRPACN 90/10	7
PVC/NRPACN 100/10	8

Figure 4 Phase-contrast micrographs of various PVC/natural rubber graft copolymer blends.
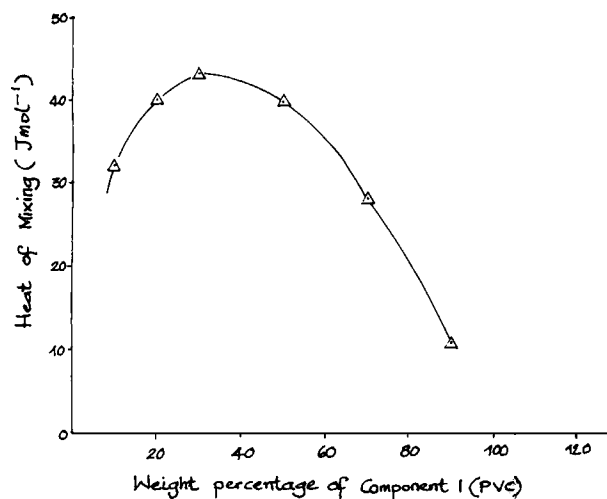
Figure 5 Heat of mixing vs. weight percentage of PVC in PVC/NRPMMA blends.

Microscopic examination of thin films of the blends were carried out with a Zeiss Ultraphot phase-contrast microscope with a video printer.

Solubility parameter of the NRPMMA sample was determined using the intrinsic viscosity method.[6] The heats of mixing of the solutions of the polymer blends were calculated from the equation[7-9]:

$$H_m = \{\bar{X}_1 M_1 \rho_1 \, (d_1 - d_2)^2 [X_2/(1 - \bar{X}_2) M_2 \rho_2$$
$$+ (1 - \bar{X}_1) M_1 \rho_1]^2\}^{1/2} \quad (1)$$

where $\bar{X}$, ρ, and M are the weight fraction of the polymer, polymer density, and the monomer unit molecular weight, respectively and d is the polymer solubility parameter.

X-ray diffraction patterns of films of PVC/NRPACN blends were achieved using a Phillips PW1729 X-ray generator using CuKα-radiation.

RESULTS AND DISCUSSION

The absolute viscosity versus weight percent composition plots for solutions of PVC/NRPACN and PVC/NRPMMA blends are shown in Figure 1. In
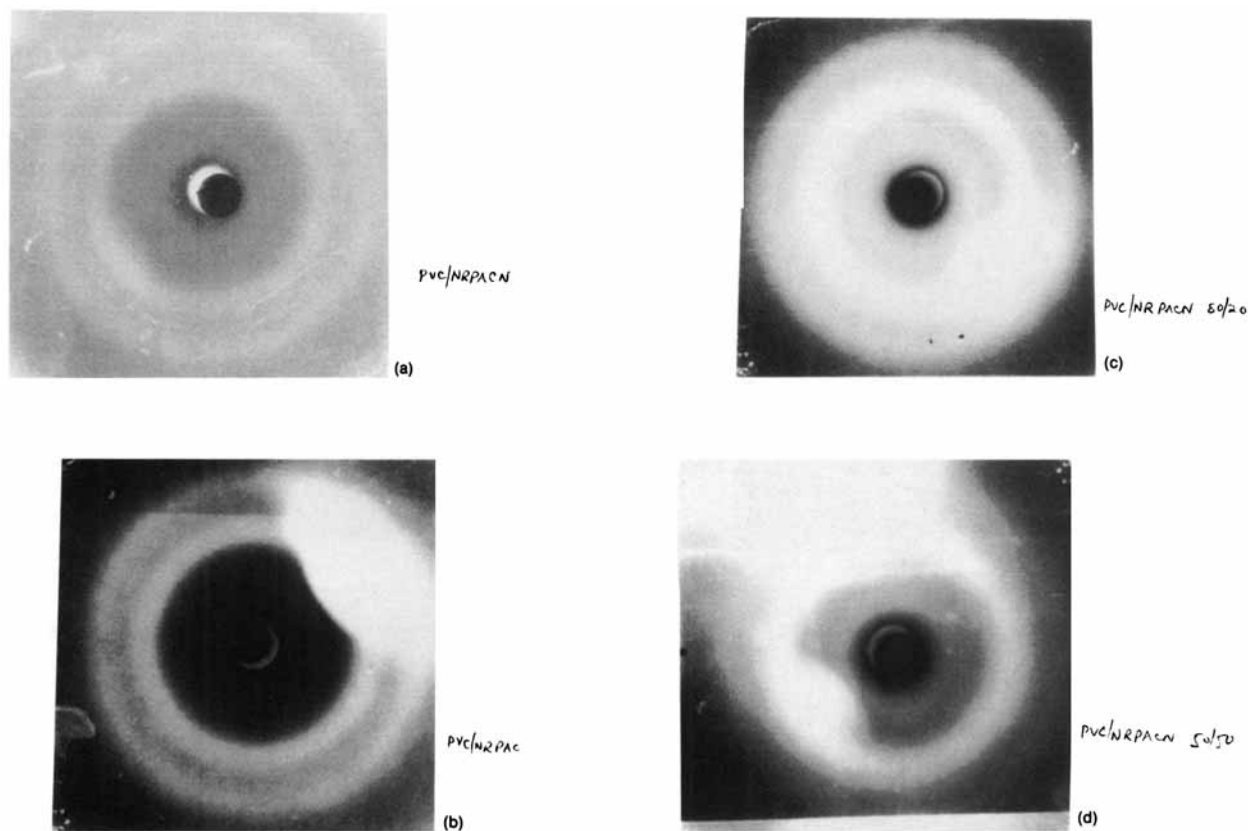

Figure 6 X-ray diffraction patterns of PVC/NRPACN blends. For sample codes 1–6, see Table III.

Table II   Sample Codes for PVC/NRPMMA Blends

Sample Code	DSC Curve
PVC/NRPMMA 0/100	1
PVC/NRPMMA 10/90	2
PVC/NRPMMA 20/80	3
PVC/NRPMMA 30/70	4
PVC/NRPMMA 50/50	5
PVC/NRPMMA 70/30	6
PVC/NRPMMA 90/10	7
PVC/NRPMMA 100/0	8

Table III   Sample Codes for PVC/NRPACN Blends

Sample Code	Picture
PVC/NRPACN 0/100	A
PVC/NRPACN 30/700	B
PVC/NRPACN 50/50	C
PVC/NRPACN 80/20	D
PVC/NRPACN 90/10	E
PVC/NRPACN 100/0	F

both cases the plots are of the inverted S-type, indicative of immiscibility of the polymers at the molecular levels. The thermal behavior of the PVC/NR graft copolymer blends were characterized by DSC. A major endothermic peak at about 265°C attributed to the melting of PVC[10,11] was observed in the DSC curve of pure PVC. This endotherm was also observed in the curves of all the blends. However, the intensity of the peak decreased somewhat when the graft copolymer content of the blends was

PVC/NRPACN

(e)

PVC/NRPACN

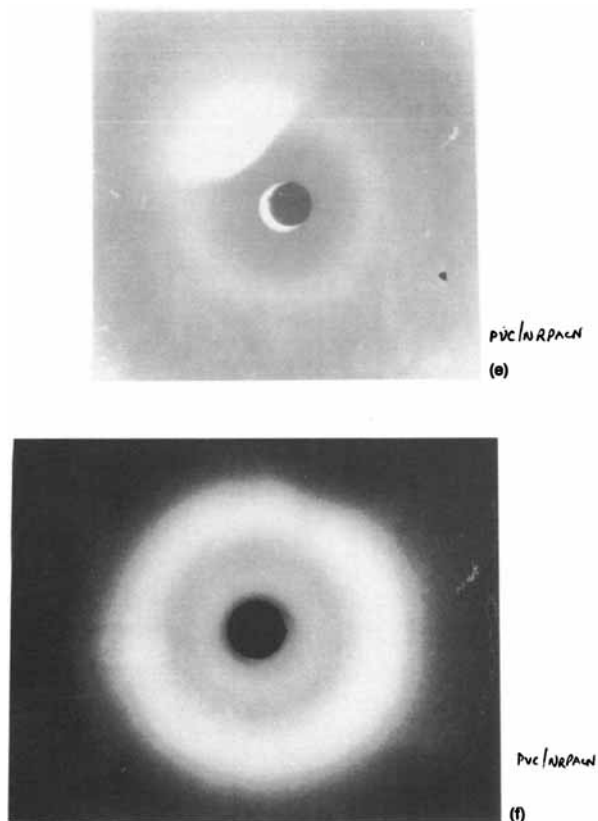(f)

Figure 6   (*Continued from the previous page*)

increased. In addition to the endotherm at about 265°C, the PVC/NRPACN blends showed a minor but broad peak at 160°–180°C for polymer blends containing between 50 and 70 wt % PVC (Fig. 2, Table I). This peak subsequently developed into two minor peaks, one about 161°C and the other about 180°C for polymer blends containing 10, 20, and 30 wt % PVC. The endotherm at about 160°–180°C was also observed in the curve of pure NRPACN. The PVC/NRPMMA blends showed a minor endotherm at about 124°C (Fig. 3, Table II). This peak was also observed in the curve of pure NRPMMA.

It is therefore suggested that the endotherms at about 160°–180°C and 124°C can be attributed to the thermal decomposition of NRPACN and NRPMMA components of the blends.

Phase-contrast micrographs of the different PVC/NRPACN blends are shown in Figure 4 and sample codes are in Table III. Gross phase discontinuity is evident in virtually all the micrographs. This observation indicates immiscibility of the polymers.

The calculated heats of mixing of the PVC/NRPMMA blends at various weight compositions of PVC are shown in Figure 5 and were found to be in the range of 10.615–43.074 J mol^{-1}. These values are well above the 4.184×10^{-2} J mol^{-1} value considered to be the upper compatibility limit,[12,13] and indicate that the polymer blends are immiscible (Fig. 5).

To detect if any changes in the crystalline structure of the polymers resulted from blending, X-ray diffraction photographs of the PVC/NRPACN blends were obtained and examined (Fig. 6). Pure PVC sample showed a less intense Debye–Scherrer ring corresponding to spacings of 4.78 and 3.26 Å. The X-ray diffraction pattern of pure NRPACN showed the spacings 4.71 and 10.36 Å. Although the blends showed a resemblence of the ring characteristic of PVC, the ring was masked by the NRPACN rings, suggesting immiscibility of the polymers.

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