

Graft Copolymerization of Acrylonitrile and Methyl Methacrylate Monomer Mixtures on Crumb Natural Rubber

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Received 22 November 2000; accepted 9 September 2001

ABSTRACT: Graft copolymerization of mixtures of acrylonitrile and methyl methacrylate on crumb natural rubber was carried out in toluene at 60°C. The nitrogen content of the grafted copolymer was determined by elemental analysis and used to estimate the composition of the copolymer samples. It was found that the amount of acrylonitrile monomeric units incorporated into the polymer was disproportionately lower than the acrylonitrile content of the feed and explanations in terms of the e -value of the monomers and the inherent heterogeneous nature of the polymerization mixture were offered. The miscibility of the natural rubber-g-polyacrylonitrile-co-poly(methyl methacrylate) with poly(vinyl chloride) was studied by viscometry, differential scanning calorimetry, and phase contrast microscopy. It was found that the natural rubber-g-polyacrylonitrile-co-poly(methyl methacrylate) formed semimiscible blends with poly(vinyl chloride). © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1872–1877, 2002; DOI 10.1002/app.10474

Key words: graft copolymerization; acrylonitrile and methyl methacrylate mixtures; crumb natural rubber; miscibility

INTRODUCTION

Natural rubber (NR) is an important renewable resource. Dry natural rubber has little or no practical use unless it is vulcanized; natural rubber does not compete favorably with rubbers of synthetic origin in areas other than the tire industry. This limitation of natural rubber is due to its poor resistance to oils and hydrocarbon solvents, high permeability to gases, high sensitivity to oxygen and ozone attack, and inconsistency in quality. These drawbacks can be alleviated by grafting with vinyl monomers. Several workers^{1–14} have

reported the preparation, characterization, and properties of copolymers of NR with acrylonitrile, methyl methacrylate, methyl vinyl ketone, styrene, methyl acrylate, and methacrylamide using a range of initiator systems. However, information on the grafting characteristics of acrylonitrile and methyl methacrylate monomer mixtures on NR is limited. In our previous study¹⁵ we examined the miscibility of NR-g-polyacrylonitrile and NR-g-poly(methyl methacrylate) with poly(vinyl chloride) (PVC). It was thought that NR containing grafted synthetic polymer chains with acrylonitrile and methyl methacrylate monomeric units could provide materials that may find application in the processing of plastic materials. This report examines the grafting characteristics of acrylonitrile (AN), and methyl methacrylate (MMA) monomer mixtures on NR and the miscibility of the NR-graft copolymer with PVC.

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Contract grant sponsor: University of Benin; contract grant number: URPC 60/489.

Journal of Applied Polymer Science, Vol. 84, 1872–1877 (2002)
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EXPERIMENTAL

Materials

NR obtained from Utagba-uno Rubber Estate, Nigeria, was extracted with acetone for 24 h. Acrylonitrile and MMA monomers (Aldrich Chemicals) were purified from hydroquinone stabilizer by extraction with aqueous alkaline solution followed by distillation. The middle fractions were collected as pure monomers. PVC (MW 200,000) obtained from BDH Ltd. was used without further purification. Benzoyl peroxide (BPO) (Aldrich Chemicals) was recrystallized from chloroform.

Methods

Graft Copolymerization

Graft copolymerization of an AN and MMA monomer mixtures on NR was carried out using the method described by Allen and Merret.² In a typical experiment, NR (93 g) was dissolved in 500 mL of toluene in a 4 L four-neck, round-bottom flask under reflux. A known amount of the monomer mixture with predetermined composition was added to the NR solution and the flask was flushed with nitrogen for 1 h. The initiator (a constant amount of initiator 0.013M was used) was then added to the reaction mixture. The reaction was allowed to proceed for 6 h and the mixture was poured into a large excess of 3.5% (w/v) formic acid solution with constant stirring. The coagulum obtained was washed thoroughly with deionized water and dried at 50°C in vacuum. The ungrafted polyacrylonitrile (PAN) and poly(methyl methacrylate) (PMMA) homopolymers were Soxhlet-extracted successively with 2,2-dimethyl formamide and acetone, respectively. The percent graft level, P_g , is reported as the weight of the material added on divided by the weight of NR multiplied by 100. The nitrogen contents of the ungrafted NR and NR graft copolymer samples were determined by the Perkin-Elmer elemental analyzer. The compositions of the NR-g-polyacrylonitrile-co-poly(methyl methacrylate) and NR-g-PAN-co-PMMA samples were worked out from their nitrogen contents using the relationship described by Okieimen and co-workers.^{16,17}

Miscibility Studies

The NR-g-PAN-co-PMMA blended with PVC contained 66 wt % PAN-co-PMMA, and 13 mole %

AN. The blends were prepared 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 solution of the polymer blends were measured at 45°C using Ubbelohde viscometer. The viscometer was first calibrated with cyclohexanone.

Differential scanning calorimetric (DSC) measurements on the blends were carried out under nitrogen using Perkin-Elmer 7 series Thermal Analysis system. Calibration was made under indium standard. The samples of the polymer blend (between 5 and 7 mg) were sealed in aluminum pans and heated at 10°C/min. Microscopic examination of thin films of the polymer blends was carried out with a Zeiss Ultraphot phase-contrast microscope with a video printer.

RESULTS AND DISCUSSION

Grafting Characteristics

The grafting characteristics of various amounts of AN and MMA on NR using a constant initiator concentration of 0.0138 mol L⁻¹ are given in Table I. The results show that the initial increase in P_g with increase in AN content of the feed reached maximum value of about 66% at 50 mole % AN and thereafter decreased with further increase in the AN content of the feed. A similar trend was observed for the graft copolymerization of AN and ethyl acrylate (EA) monomer mixtures on starch.¹⁸ During graft polymerization of AN and MMA mixtures on NR in toluene solution, phase separation may occur even at low monomer conversions. For instance, PAN being insoluble in aromatic solvents, graft copolymerization segments rich in PAN may precipitate. The monomers will consequently be partitioned between the polymer-rich phase and the continuous solvent phase. It is thought that the relative miscibility of the monomers in the polymer-rich phase will affect monomer concentration at the loci of graft polymer formation and hence influence the level of grafting. This change in the physical nature of the graft polymerization system may be responsible for the observed grafting characteristics of AN and MMA monomer mixtures on natural rubber.

Graft Copolymer Composition

The nitrogen contents and the composition of the grafted copolymer samples are shown in Figure 1

Table I Grafting Characteristics of Acrylonitrile and Methyl Methacrylate Monomer on Natural Rubber at 60°C using 0.0138M Benzoyl Peroxide

Feed Composition (Mole Fraction AN) f	Weight of Coagulum (g)	Weight of Homopolymers (g)		Weight of Grafted Copolymer (g)	P_g (%)
		PAN	PMMA		
0.384	6.66	0.43	1.99	1.23	41.00
0.423	6.44	0.48	1.40	1.56	52.00
0.461	5.91	0.54	1.11	1.26	42.00
0.500	6.57	0.53	1.07	1.97	65.67
0.537	5.91	0.63	0.69	1.58	52.67
0.576	6.12	1.08	0.73	1.30	43.33
0.615	5.94	1.29	0.60	1.05	35.00

as a function of the monomer feed composition. It can be seen that although there is a general increase in the AN content of the copolymer samples with increase in the proportion of AN in the feed, the amount of AN monomeric units incorporated in the copolymer samples are disproportionately lower than the AN content of the feed. A similar trend was observed for the graft copolymerization of binary vinyl monomer mixtures on cellulose,¹⁹ starch,¹⁶ carboxymethyl cellulose,¹⁷

and dextrin.¹⁸ In addition to the physical state of the polymerization system, the electronic charge (e-value) is an important factor that may affect monomer reactivity in radical polymerization: monomer with relatively high e-value will produce radicals that are relatively less reactive toward propagation.²⁰ The e-value of AN is three-fold higher than value for MMA.²¹ It may therefore be expected that AN radicals will react relatively less readily than radicals derived from MMA in graft polymer formation. The monomer reactivity ratios estimated from the copolymer composition using Fineman and Ross method,²² although providing only rough estimates, for AN and MMA were found to be $r_1 = 0.56$ and $r_2 = 1.5$, suggesting that self-propagation of AN monomeric units is low.

Miscibility Studies

The miscibility behavior of NR-g-PAN-co-PMMA with PVC was studied by viscometry, DSC, and phase-contrast microscopy. The variation of absolute viscosity measured at 45°C with the composition of the polymer blend is shown in Figure 2. It can be seen that plot is neither linear nor of the inverted S-type. This might be thought to suggest miscibility within a limited range of the polymer blend composition.¹⁵

The DSC curves of pure PVC showed a major endotherm at about 265°C. A peak at about this temperature which increased in width as the NR-g-PAN-co-PMMA content increased was observed in all the blends (Fig. 3). In addition to the endotherm at 265°C, two minor peaks, one about 207–210°C and the other about 220°C were observed for blends containing less than 50 wt % PVC (curves 2–4). These peaks were not observed for

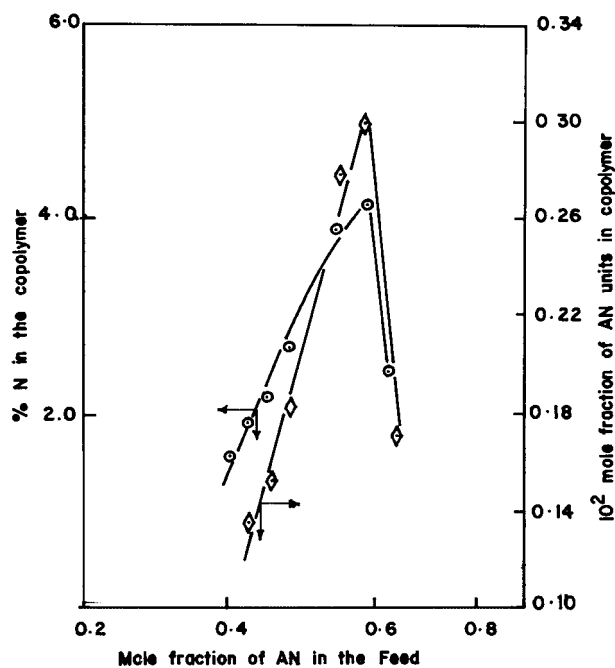


Figure 1 Grafting AN and MMA monomer mixtures on natural rubber. Variations of nitrogen content of the graft copolymer and copolymer composition with monomer feed composition.

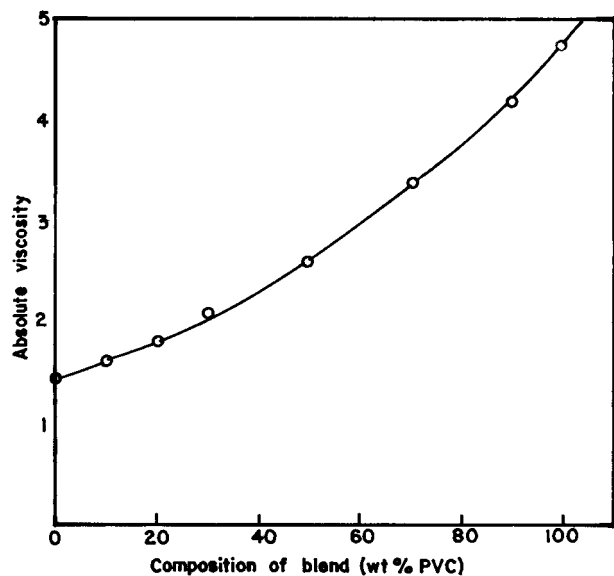


Figure 2 Absolute viscosity vs composition of NR-g-polyacrylonitrile-co-poly(methyl methacrylate) PVC blends at 45°C.

PVC and are ascribed to the NR-g-PAN-co-PMMA component of the blend. It can be seen in Figure 3 that the peaks due to the NR-g-PAN-co-PMMA

component of the blend were not observed in the blends containing 70 and 90 wt % PVC (curves 5 and 6). This suggests some level of miscibility at these compositions.

Phase-contrast micrographs of the different blend compositions are shown in Figure 4. It can be seen that although phase discontinuity is evident in the blends containing 30 and 50 wt % PVC (pictures B and C), the discontinuities are less discernible in blends containing 70 and 90 wt % PVC (pictures D and E). These observations suggest that NR-g-PAN-co-PMMA shows limited solubility with PVC.

This study has provided some information on the relative reactivity of AN and MMA monomer toward grafting onto NR, and showed that the NR-g-PAN-co-PMMA was miscible with PVC at blend compositions containing more than 70 wt % PVC.

Part of this work was carried out in the H. H. Willis Physical Laboratory of the University of Bristol, UK, while INU was on World Bank loan sponsored research leave. The assistance of Dr. Jeff A. Odell is gratefully acknowledged. The authors are grateful to the University of Benin for Research Grant URPC 60/489 to FEO.

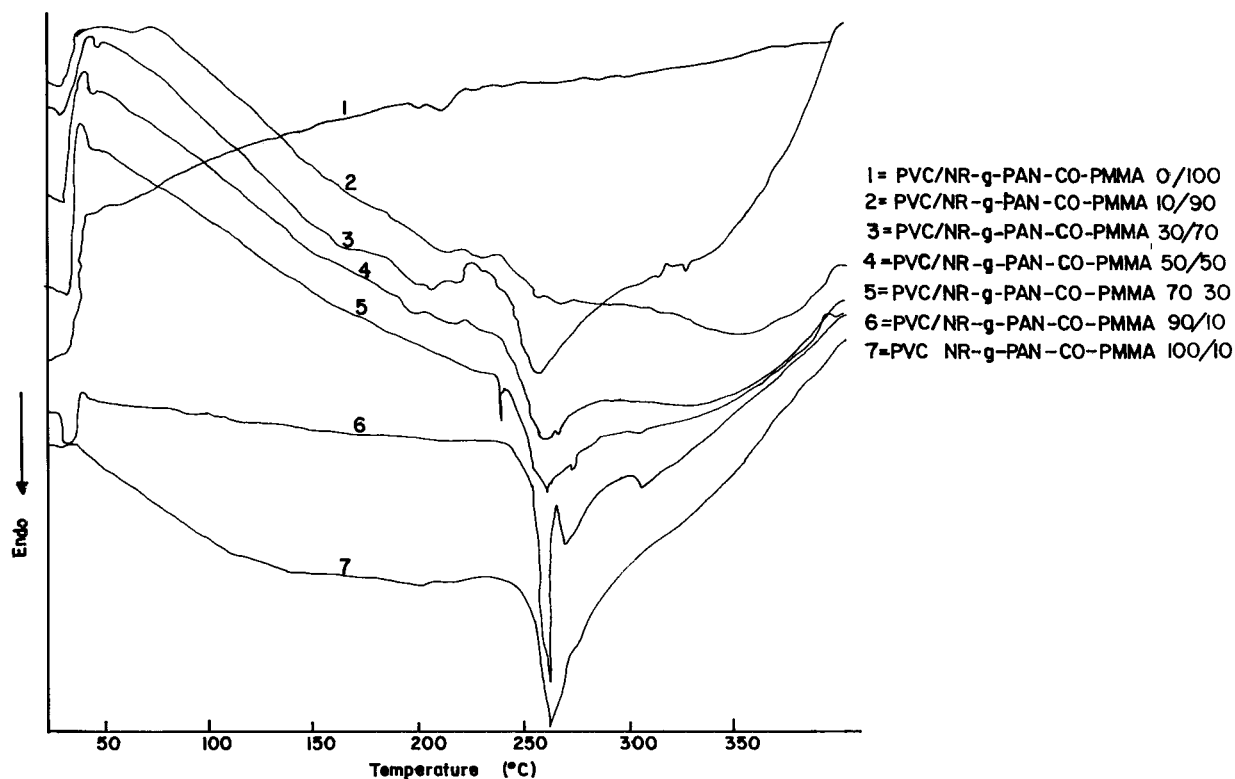


Figure 3 DSC curves of PVC/NR-g-PAN-co-PMMA.

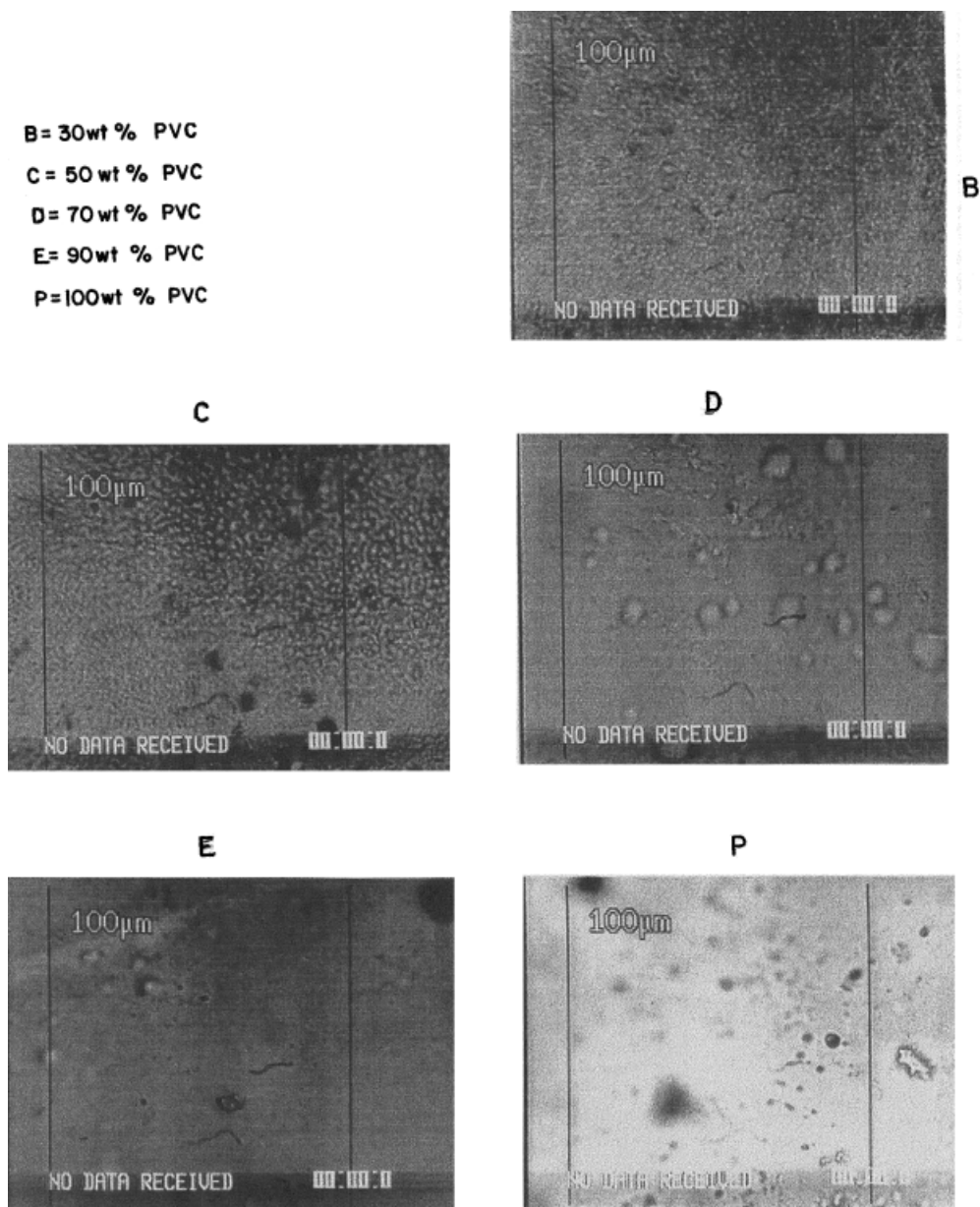


Figure 4 Phase-contrast micrographs of PVC/NR-g-PAN-co-PMMA blends.

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