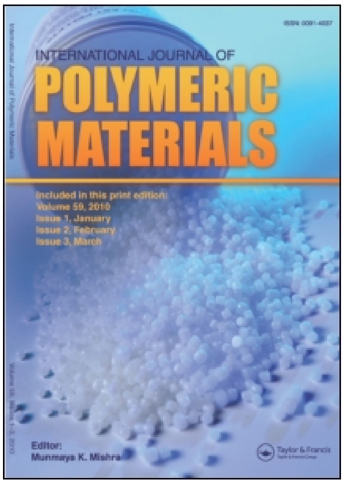


International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

^{1}HNMR and FTIR Spectroscopic Studies on the Blends of Polychloroprene with Polyethylene Vinylacetate

P. P. Kundu[a]; S. Banerjee[b]; D. K. Tripathy[a]
[a] Rubber Technology Centre, Indian Institute of Technology, Kharagpur, India [b] Defence Research & Development Establishment, DRDO, Gwalior, India

To cite this Article Kundu, P. P. , Banerjee, S. and Tripathy, D. K.(1996) '^{1}HNMR and FTIR Spectroscopic Studies on the Blends of Polychloroprene with Polyethylene Vinylacetate', International Journal of Polymeric Materials, 32: 1, 125 — 134

To link to this Article: DOI: 10.1080/00914039608029389

URL: http://dx.doi.org/10.1080/00914039608029389

Intern. J. Polymeric Mater., 1996, Vol. 32, pp. 125–134
Reprints available directly from the publisher
Photocopying permitted by license only

Amsterdam B.V. Published in The Netherlands
under license by Gordon and Breach Science
Publishers SA
Printed in Malaysia

^{1}HNMR and FTIR Spectroscopic Studies on the Blends of Polychloroprene with Polyethylene Vinylacetate

P. P. KUNDU,† S. BANERJEE‡ and D. K. TRIPATHY†,*

†Rubber Technology Centre, Indian Institute of Technology, Kharagpur 721302, India;
‡Defence Research & Development Establishment, DRDO, Jhansi Road, Gwalior 474002, India

(Received May 10, 1995)

The ratio of different protons obtained from the integrated peak areas of solution ^{1}HNMR signals tallies with the calculated values obtained from macroblend composition. ^{1}HNMR results indicate that the blends of polychloroprene (CR) with polyethylene vinylacetate (EVAc) shows homogenity in mixing throughout their entire compositions. The increase in absorption frequency for C—O—C asymmetric stretching with increased contents of CR in the EVAc/CR blends indicates dipolar interactions between polar vinylacetate and chloride groups.

KEY WORDS Polyethylene vinylacetate, polychloroprene, ^{1}HNMR, FTIR, blend composition, homogenity, dipolar interactions.

INTRODUCTION

Proton Nuclear Magnetic Resonance (^{1}HNMR)[1-3] and Fourier Transform Infra Red (FTIR)[4-6] spectra are two important tools for characterisation of polymers and their blends.

It is reported that early studies on polymers using solid state NMR give rise to broad band spectra. These were almost always proton spectra. Their width and shape are related to spin-lattice and spin-spin relaxations.[7,8] The NMR spectra of polymers in solution show narrow response lines which reveal detailed information about their structure.

Although miscibility can be studied with magic angle spinning NMR[9,10] (MAS NMR), broad response lines can not show detailed structure of the polymers in their blends. In contrast polymeric blends in solution can give rise to detailed structure as well as a quantitative measure of segmental mixing[11] through the integrated peak areas of different proton resonances.

The high resolution FTIR spectra of any substance is interpreted by the use of known functional group frequencies which are associated with certain characteristic

---

*Corresponding author.

TABLE I

Details of materials used

Material	Specification*	Producer
Poly(ethylenevinyl acetate) (Pilene 2806)	Vinyl acetate: 28 wt. % Density: 0.95 gm/cm^3 M.F.I.: 6 g/10 min	Polyolefin Industries Ltd., India
Poly(ethylenevinyl acetate) (Laevaprene-450)	Vinyl acetate: 45 wt. % Specific gravity: 0.98 Mooney viscosity: 20 (ML_{1+4}, 100°C)	Bayer AG, Germany
Polychloroprene (Neoprene WM1)	Specific gravity: 1.23 Mooney viscosity: 40 (ML_{1+4}, 100°C)	duPont, USA

*As supplied by the producers.

TABLE II

Blend composition (wt. %)

Component	A	B	C	D	E	F	G	H	I
EVAc-28	100	70	50	30	—	—	—	—	—
EVAc-45	—	—	—	—	—	100	70	50	30
CR	—	30	50	70	100	—	30	50	70

absorption bands.[12] The functional groups present in polymers can be identified with FTIR. In case of polymeric blends, the individual group frequencies may remain intact or shift in definite directions, leading to non-interactive and interactive polymeric blends respectively. For a miscible polymeric blend, FTIR provides a tool for qualitative measurement of their miscibility.[13,14]

It is found that blends of polychloroprene (CR) with polyethylene vinylacetate (EVAc)[15,16] are miscible. The present paper deals with the spectroscopic studies of EVAc/CR blends through ^{1}HNMR and FTIR in order to find out their phase homogenity and specific interaction.

EXPERIMENTAL

Materials Used

The details of materials used are given in Table I.

Sample Preparation

The polymers were mixed in a Brabender Plasticorder (PLE-330) provided with a cam type rotor as in the formulation given in Table II. Thermoplastic polymer was first melted at 100°C for 2 minutes and then mixed with premasticated neoprene. To ensure proper mixing, the blending was done at 100 rpm and at 100°C for 5 minutes. The hot blend was taken out and then sheeted out through a low nip gap two-roll mill. Very thin sheets (0.5 mm) for FTIR were moulded at 100°C and at 1 MPa. The

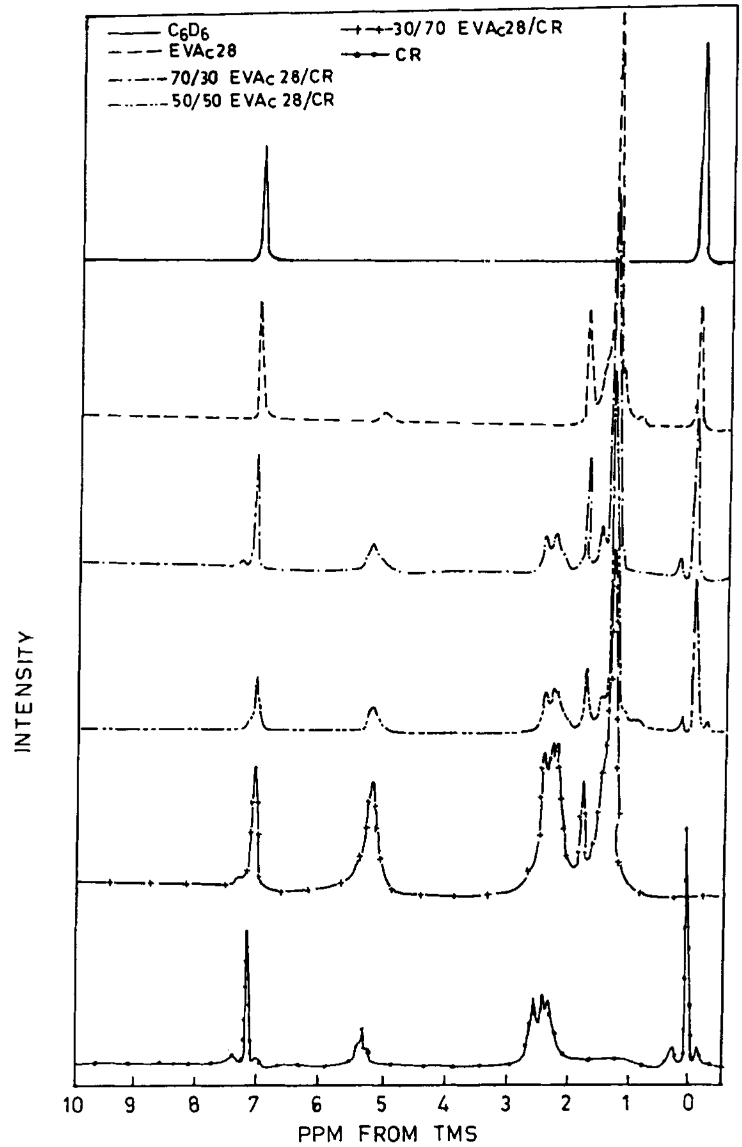


FIGURE 1 Plots of proton NMR vs. intensity for EVAc-28/CR blends.

infrared spectroscopy was carried out using a Perkin Elmer FTIR-1720X Spectrophotometer equipped with an DTGS detector and a flat plate ATR sampling accessory, KRS-5 parallelogram crystal with an angle of incident of 45°. All the ATR spectra were collected at 4 cm^{-1} resolution and 20 scans were accumulated for each sample.

A fairly concentrated solution of all samples in deuterated benzene was taken in a sample cell and placed in a JEOL, 90 MHz, FT-NMR for proton nuclear magnetic resonance characterisation.

TABLE III

^{1}HNMR results of EVAc-28/CR blends

Blend	^{1}HNMR signal, δ in ppm of the protons of			Number of protons from peak intensity			Molar segment ratio of EVAc-28	Number of protons from molar segment ratio		
code	CH_2	CH	CH_3	CH_2	CH	CH_3	and CR	CH_2	CH	CH_3
A	0.9–1.5	5.0–5.2	1.7–2.0	31.4	1.0	3.0	—	31.4*	1.0*	3.0*
B	0.9–1.5, 2.1–2.6	5.0–5.4	1.7–2.0	15.4	1.0	1.3	85:15	15.0	1.0	1.2
C	0.9–1.5, 2.1–2.6	5.0–5.4	1.7–2.0	14.1	1.3	1.0	72:28	14.7	1.4	1.0
D	0.9–1.5, 2.1–2.6	5.0–5.4	1.7–2.0	20.4	2.7	1.0	52:48	20.4	2.8	1.0
E	2.1–2.6	5.1–5.4	—	4.0	1.0	—	—	4.0	1.0	—

*Calculated from 88:12 molar segment ratio of ethylene and vinyl acetate.

RESULTS AND DISCUSSION

The plots of proton signal for pure solvent C_6D_6, CR, EVAc-28 and 70/30, 50/50 and 30/70 EVAc-28/CR blends are shown in Figure 1 and their corresponding shift and area values are given in Table III. The peak at 7.1 ppm is assigned to benzene proton signal (C_6D_5H) due to the absorption of water by C_6D_6. This benzene peak is present in every sample. The triplet proton signals at 5.1–5.4 ppm and quartet at 2.1–2.6 ppm are associated with $=$CH and —CH_2— protons of CR respectively.[17]

The broad peak at 5.0–5.2 ppm, the triplet at 1.7–2.0 ppm and multiplet at 0.9–1.5 ppm are due to —CH$=$, —OCH_3 and —CH_2— protons present in EVAc-28 respectively.[18–20]

All blends show the characteristic proton signals of CR and EVAc-28. The number of CH_2, CH and CH_3 protons calculated from peak intensities and macroblend composition are given in Table III. The detailed calculation for different protons present in the blend are shown in Appendix 1. The ratio of integrated peak areas or intensities for CH_2, CH and CH_3 as given by 15.4:1.0:1.3 are found to match well with the calculated ratio of 15.0:1.0:1.2 for 70/30 EVAc-28/CR blend.

In case of 50/50 and 30/70 EVAc-28/CR blends, the calculated ratios of CH_2, CH and CH_3 protons are 14.7:1.4:1.0 and 20.4:2.8:1.0 respectively and these are in accordance with their ratios of 14.1:1.3:1.0 and 20.4:2.7:1.0 as obtained from integrated peak areas of ^{1}HNMR (Table III).

The calculated ratios of CH_2, CH and CH_3 protons match well with those of integrated area from ^{1}HNMR, and remains same for different ^{1}HNMR signals of different sets of all the EVAc/CR blends. Thus the results reveal that both EVAc and CR are mixed homogeneously in the blends. This homogeneous mixing is also confirmed by single glass transition of the blends.[15]

The plots of ^{1}HNMR signals for EVAc-45, 70/30, 50/50 and 30/70 EVAc-45/CR blends are shown in Figure 2. The number of CH_2, CH and CH_3 protons calculated from blend composition as well as found from integrated peak areas of ^{1}HNMR are given in Table IV. The ratios of CH_2, CH and CH_3 protons present in 70/30, 50/50

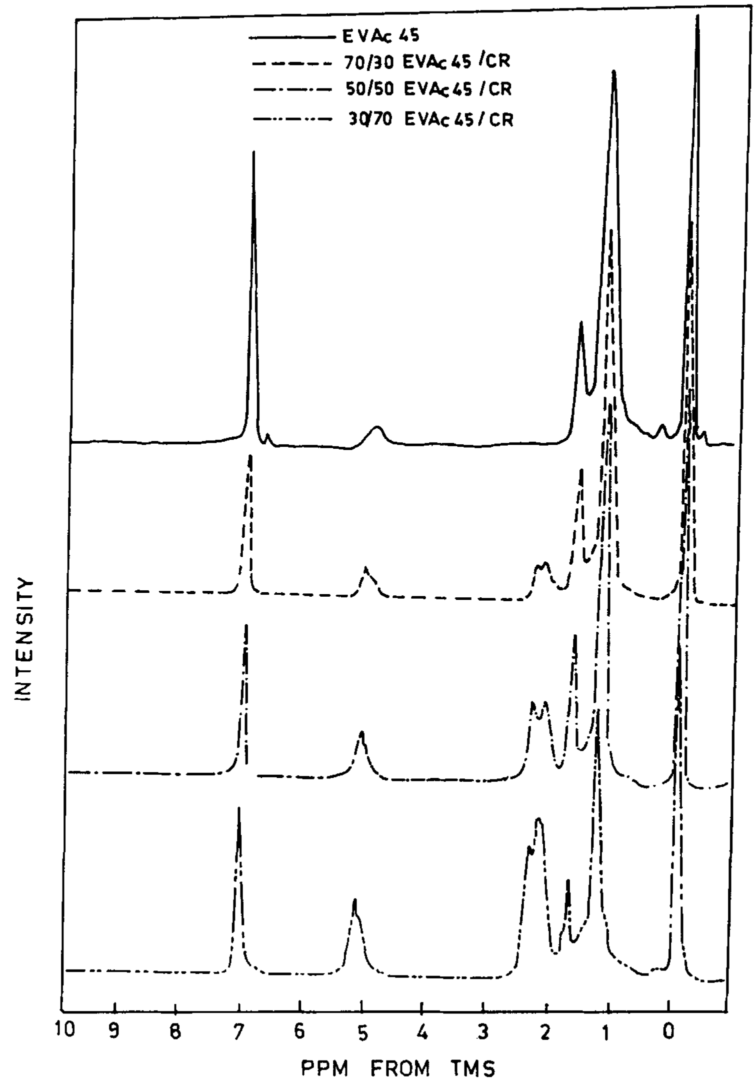


FIGURE 2 Plots of proton NMR vs. intensity for EVAc-45/CR blends.

and 30/70 EVAc-45/CR blends are 10.7:1.0:1.6, 8.4:1.1:1.0 and 12.2:2.0:1.0 respectively and these are in close agreement with the ratios 10.6:1.0:1.6, 8.2:1.1:1.0 and 12.5:2.0:1.0 as obtained from the peak intensities of ^{1}HNMR. These results indicate that EVAc-45 and CR are mixed homogeneously which is also confirmed by their single glass transitions.[16]

The FTIR absorption spectra of EVAc-28, CR, 70/30, 50/50 and 30/70 EVAc-28/CR blends are shown in Figure 3 and their characteristic group absorption bands are given in Table V. The absorption band at 1309 cm^{-1} is due to the CH in plane deformation of C=C group of CR.[12] The band at 1451 cm^{-1} is due to C—Cl overtone frequency. The band at 1236 cm^{-1} is assigned to the C—O—C asymmetric

TABLE IV

^{1}HNMR results of EVAc-45/CR blends

Blend code	^{1}HNMR signal, δ in ppm of the protons of			Number of protons from peak intensity			Molar segment ratio of EVAc-45 and CR	Number of protons from molar segment ratio		
	CH_2	CH	CH_3	CH_2	CH	CH_3		CH_2	CH	CH_3
F	0.9–1.5	5.0–5.2	1.7–2.0	17.0	1.0	3.0	—	17.0*	1.0*	3.0*
G	0.9–1.5, 2.1–2.6	5.0–5.4	1.7–2.0	10.6	1.0	1.6	84:16	10.7	1.0	1.6
H	0.9–1.5, 2.1–2.6	5.0–5.4	1.7–2.0	8.2	1.1	1.0	69:31	8.4	1.1	1.6
I	0.9–1.5, 2.1–2.6	5.0–5.4	1.7–2.0	12.5	2.0	1.0	49:51	12.2	2.0	1.0

*Calculated from 79:21 molar segment ratio of ethylene and vinyl acetate.

stretching vibration of EVAc-28. The carbonyl (>C═O) characteristic stretching band is at 1735 cm^{-1}.

The characteristic C—O—C asymmetric stretching frequency of EVAc-28 is shifted to 1240, 1242 and 1243 cm^{-1} for 70/30, 50/50 and 30/70 EVAc-28/CR blends. This may be attributed to the increased dipolar interaction between EVAc-28 and CR as shown in the Scheme I.

FTIR absorption spectra of EVAc-45, 70/30, 50/50 and 30/70 EVAc/CR blends are shown in Figure 4 and their characteristic bands are given in Table VI. The characteristic bands at 1735 and 1230 cm^{-1} are due to carbonyl and C—O—C asymmetric stretching frequency of EVAc-45. The band at 1230 cm^{-1} is shifted to 1236, 1240 and 1241 cm^{-1} by blending with 30, 50 and 70% CR. The reason for these shifts is same as in case of EVAc-28 and CR blends.

CONCLUSIONS

The following conclusion can be drawn from the above studies:

(a) ^{1}HNMR results show that the number of CH_2, CH and CH_3 protons present in the molecular segments of EVAc/CR blends calculated on the basis of macroblend compositions are in close agreement with those obtained from their integrated peak areas of ^{1}HNMR signals. This indicates their phase homogenity over their entire compositions.

(b) FTIR results show that shifting of the absorption frequency for the C—O—C asymmetric stretching vibration of EVAc increases with increased content of CR in the EVAc/CR blends.

(c) Based on the ^{1}HNMR and FTIR spectroscopic studies, it can be concluded that all the blends are well mixed and there exists dipolar interactions between the blended polymers.

(d) This phase homogenity and dipolar interactions coupled with the earlier reported[15,16] single glass transition temperatures of EVAc and CR blends reveals their miscibility.

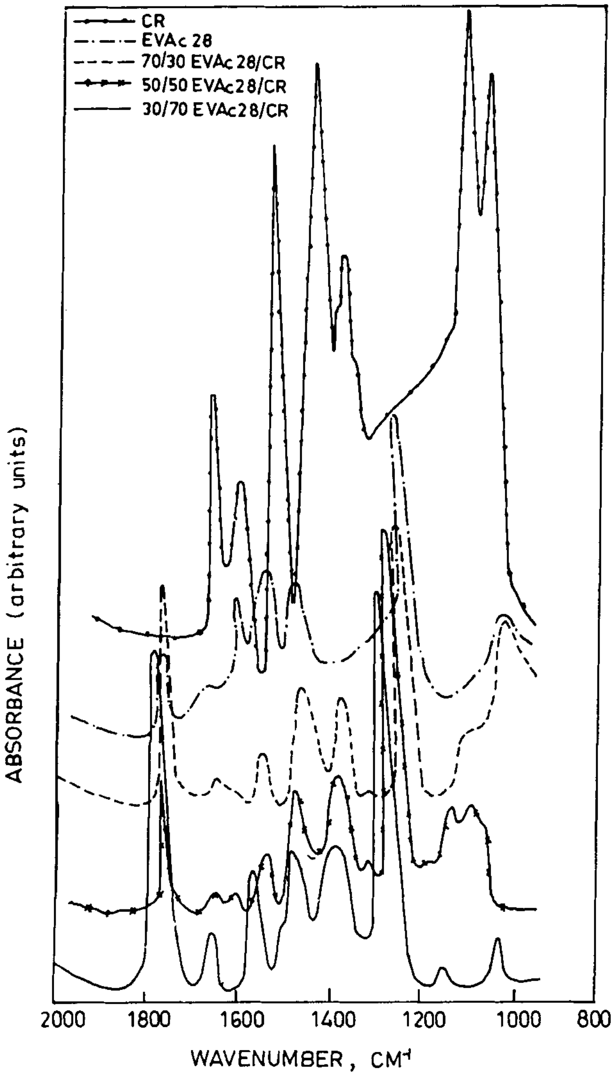


FIGURE 3 FTIR plots of wave number in cm^{-1} vs. absorbance in percent for EVAc-28/CR blends.

APPENDIX 1

Let us consider two polymers A and B with a blend composition of x and y gms respectively. If polymer A is copolymer like EVAc, the molar ratios of copolymer components can be calculated from the known weight ratios of copolymer components e.g. 28% vinylacetate content in EVAc-28. Then segmental molecular weight M_1 and M_2 of respective copolymer A and homopolymer B can be calculated from their single monomeric unit. The molefraction of segments for each component A and B can be calculated from their blend ratio $x:y$ as follows:

Let, p $(=x/M_1)$ and q $(=y/M_2)$ moles of A and B respectively are present in the blend. Then their molefractions are $p/(p+q)$ and $q/(p+q)$.

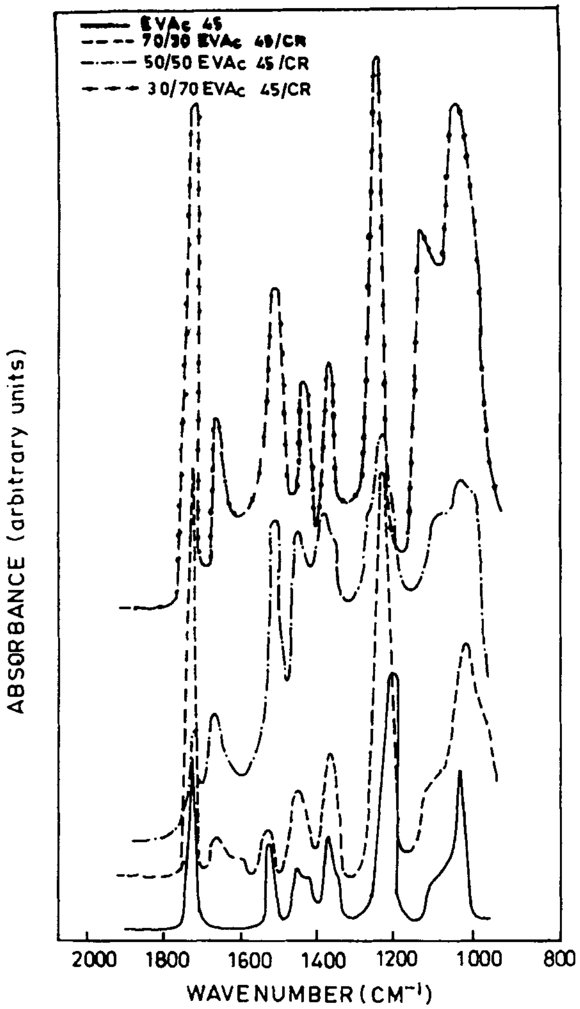
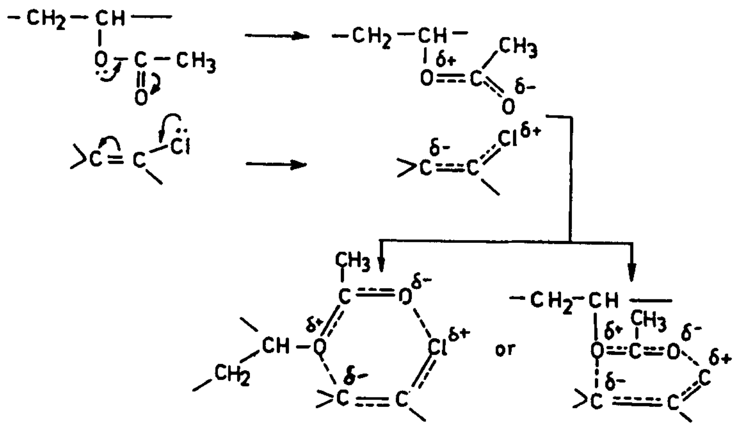


FIGURE 4 FTIR plots of wave number in cm^{-1} vs. absorbance in percent for EVAc-45/CR blends.

TABLE V

Major FTIR peaks present in EVAc-28/CR blends

Frequency	EVAc-28	EVAc-28/CR blends			CR
		70/30	50/50	30/70	
C—O—C asymmetric stretch (cm^{-1})	1236	1238	1240	1241	—
>C=O stretch (cm^{-1})	1735	1735	1735	1735	—
C—Cl overtone (cm^{-1})	—	1451	1451	1451	1451
>C=C< stretch (cm^{-1})	—	1659	1659	1659	1659



SCHEME I

TABLE VI

Major FTIR peaks present in EVAc-45/CR blends

Frequency	EVAc-45	EVAc-45/CR blends 70/30	50/50	30/70
C—O—C stretch (cm^{-1})	1230	1236	1240	1241
>C=O stretch (cm^{-1})	1735	1735	1735	1735
C—Cl overtone (cm^{-1})	—	1451	1451	1451
C=C stretch (cm^{-1})	—	1658	1658	1658

Thus, segment ratios of copolymer components of polymer A and segment ratios of A and B in their blends are known. The number of CH_2, CH and CH_3 protons present in the blend system can be calculated.

Let us consider a specific case of 50/50 blend of EVAc-28 and CR. Segment ratios of ethylene and vinyl acetate in EVAc-28 and EVAc-28 and CR in the blend are calculated as 0.88:0.12 and 0.72:0.28 respectively. Total number of CH_2, CH and CH_3 protons present in molecular segments of EVAc and CR in the blend are calculated as 3.83, 0.37 and 0.26 in the ratio of 14.7:1.4:1.0 respectively.

References

1. M. M. Coleman and E. G. Brame, *Rubber Chem. Technol.*, **51**, 669 (1978).
2. F. A. Bovey, L. Jelinski and P. A. Mirau, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, Inc., 1988.
3. T. K. Kwei, Y. K. Dai, X. Lu and R. A. Weiss, *Macromolecules*, **26**, 6583 (1993).
4. Y. Xu, J. Graft, P. C. Painter and M. M. Coleman, *Polymer*, **32**, 3103 (1991).
5. K. J. Zhu, S. F. Chen, T. Ho, E. M. Pearce and T. K. Kwei, *Macromolecules*, **23**, 150 (1990).
6. M. M. Coleman, D. F. Varnell and J. P. Runt, in "Polymer Alloys-III," Eds., D. Klempner and K. C. Frich, Plenum Press, New York, 1981.
7. T. Nishi, *Rubber Chem. Technol.*, **51**, 1075 (1978).
8. A. Simmons and A. Natansohn, *Macromolecules*, **23**, 5127 (1990).

9. J. B. Miller, K. J. McGrath, C. M. Roland, C. A. Trask and A. N. Garroway, *Macromolecules*, **23**, 4543 (1990).
10. M. B. Djorljevic and R. S. Porter, *Polym. Eng. Sci.*, **22**, 1109 (1982).
11. C. Y. Chu, K. N. Watson and R. Vukov, *Rubber Chem. Technol.*, **60**, 636 (1987).
12. G. Socrates, "Infrared Characteristic Group Frequencies," Wiley, New York, 1980.
13. E. J. Moskala, D. F. Varnell and M. M. Coleman, *Polymer*, **26**, 228 (1985).
14. L. C. Cesteros, J. R. Isasi and I. Katime, *Macromolecules*, **26**, 7256 (1993).
15. P. P. Kundu, B. K. Samanta Roy and D. K. Tripathy, *Polymer Networks and Blends* **5**, 11 (1995).
16. P. P. Kundu and D. K. Tripathy, *Kautsch. Gummi Kunstst.* (communicated).
17. R. C. Ferguson, *Rubber Chem. Technol.*, **40**, 385 (1967).
18. H. Y. Chen, *Rubber Chem. Technol.*, **41**, 47 (1968).
19. F. A. Bovey, M. D. Bruch and S. A. Kozlowski, *Macromolecules*, **18**, 1418 (1985).
20. S. Kole, P. P. De and D. K. Tripathy, *Polymer*, **34**, 3732 (1993).