Journal of Thermal Analysis and Calorimetry, Vol. 58 (1999) 509-515

THERMAL CHARACTERIZATION OF VINYL ACETATE–ETHYLENE COPOLYMERS

N. Gupta[1], *R. K. Srivastava*[1], *V. Choudhary*[1], *I. K. Varma*[1] *and*
S. Patnaik[2]

[1]Centre for Polymer Science and Engineering, Indian Institute of Technology, Hauz Khas
New Delhi-110 016
[2]H. M. G. Industries Ltd. (Chemical Division) Andheri (East), Mumbai- 400 059, India

(Received October 1, 1998)

Abstract

Copolymers of vinyl acetate and ethylene were prepared by emulsion polymerization using ammonium persulphate and sodium metabisulphite as initiators in presence of cyclohexane. Several copolymer samples were prepared by changing initial pressure of ethylene from 100 to 250 psi. The copolymer composition was determined by ^{1}H-NMR and thermogravimetric analysis in nitrogen atmosphere.

Keywords: copolymers, emulsion polymerisation, vinyl acetate-ethylene

Introduction

Poly(vinyl acetate) is a hard, brittle material with a T_g of 32°C and has only limited applications at room temperature. In order to extend its potential application areas, flexibility is imparted to it by plasticization which is achieved either by (a) addition of a plasticizer or (b) copolymerization with an appropriate comonomer (internal plasticisation). The disadvantage of external plasticisation is poor performance (long term) of the polymer due to the possibility of leaching or migration of plasticiser.

The problem can be eliminated by copolymerization of vinyl acetate with appropriate comonomers to impart desired flexibility and reduction in T_g to $\approx$0°C. Such copolymers are used in paint, adhesives and coatings [1, 2]. Several comonomers such as 1-decene, ethylene, butyl acrylate have been used for this purpose. Amongst these ethylene is most efficient comonomer as it increases toughness, flexibility and serviceability of copolymers. Therefore, copolymers of vinyl acetate–ethylene (VAE) having high vinyl acetate content have been extensively investigated in the past [3].

Quantitative determination of vinyl acetate content in these copolymers has been carried out using chemical methods (i.e. acetoxy-hydroxyl transformation) [4, 5] and instrumental methods (pyrolysis gas chromatography [6], thermogravimetry

1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

[7, 8], elemental analysis [9], ^{1}H-NMR [10–14]). However all these methods have been used with copolymers having high ethylene content (EVA). When vinyl acetate content is high, some of these techniques give erratic results. ^{1}H-NMR is considered to be the best method [2] for characterization.

Thermogravimetry is a useful technique to monitor loss of acetic acid on thermal degradation of poly(vinyl acetate) and may be used to determine copolymer composition of VAE. No systematic studies have been reported for correlating vinyl acetate content of VAE copolymers estimated by ^{1}H-NMR and thermogravimetric analysis of such copolymers. The present studies focus on this aspect. VAE copolymers with varying ethylene content were prepared by emulsion polymerisation using different initial pressures of ethylene or different cyclohexane content.

Experimental

Materials

Vinyl acetate monomer (VAM Organic Chemicals Ltd.) was washed with 5% aq. sodium hydroxide solution to remove hydroquinone inhibitor. The monomer was further purified by distillation at 72°C. Commercially available ethylene (SMS Multi Tech), sodium dodecyl benzene sulphonate paste (SDD paste, VAM Organic Chemicals Ltd.), hydroxyethyl cellulose (nitrosol LR, nitrosol GR), nonyl phenyl ethylene oxide condensate 10 and 30% (NP-10, NP-30), poly(vinyl alcohol), ammonium persulphate (APS), sodium metabisulphite (SMS), sodium bicarbonate (all from S.D. Fine Chemicals Ltd.) and cyclohexane (Merck) were used as received. Distilled water was used for carrying out emulsion polymerisation.

Techniques

Gravimetry was used to determine percent solids of emulsion copolymers. Approximately 5 g of latex was placed into a preweighed petridish. The latex sample was then dried at 80°C for 12 h in a vacuum oven. Once a constant mass of dried sample was obtained, the percent solid could be calculated.

Copolymer composition was determined by ^{1}H-NMR using a Bruker AC 300 MHz spectrometer, $CDCl_3$ as a solvent and TMS as an internal standard.

A DuPont 2100 thermal analyser having 951 TG module was used for thermal characterization in nitrogen atmosphere (flow rate – 60 cm^3 min^{-1}). A sample mass of 11±2 mg and heating rate of 10°C min^{-1} was used.

Gel content was determined by coagulating the latex using saturated $MgSO_4$ solution. The precipitated polymer was filtered and washed thoroughly with distilled water. The sample was dried in a vacuum oven at 80°C for 12 h. Accurately weighed (≈1.0 g) polymer sample was then added to toluene (100 mL) and left overnight for dissolution. The solution was warmed to ~60°C for 15–20 min and then gel portion was removed by filtration through a sieving cloth into a preweighed 250 mL beaker. The solution was concentrated by heating and finally the beaker was placed in an oven at 80°C for 12 h. After cooling in a desiccator the contents were weighed and gel content was determined.

Emulsion polymerisation

A Parr reaction kettle (1 litre, model No. 4842) was used to carry out the polymerization. The conditions used are given in Table 1. Emulsifiers (i.e. SDD paste, Nitrosol LR, Nitrosol GR NP-10, NP-30 and PVA solution) and $NaHCO_3$ and requisite amount of cyclohexane were charged initially. After the autoclave head was secured, the initiators and vinyl acetate (VAc) were charged in four intervals. Nitrogen was bubbled slowly through the charge for 5 min. The contents were agitated at 130 rpm and the temperature was raised to 40°C. Initial ethylene pressure (varying from 100–250 psi) was then applied. While the temperature of the charge was equilibrating, 4 mL APS (6.5% w/v) followed by 4 mL SMS (6.5% w/v) solution were charged into the reactor using nitrogen gas pressure.

Table 1 Preparation of vinyl acetate–ethylene copolymers: conditions of copolymerization

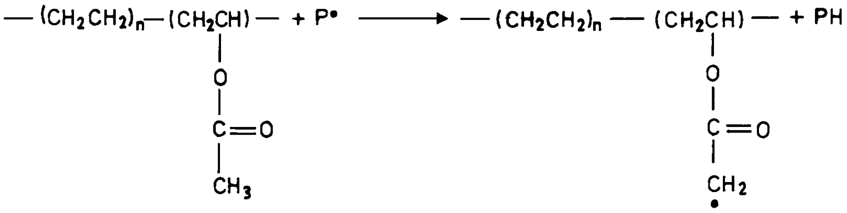
No.	Sample designation	Initial pressure of ethylene/psi	Cyclohexane/g
1.	714	250	6.0
2.	716	250	9.0
3.	723	150	6.0
4.	724	100	6.0
5.	908	0	0.0

Vinyl acetate: 100 mL; sodium dodecyl benzene sulphonate (SDD Paste): 4.0 g; NP 10: 1.0 g, NP 30: 4.0 g; Nitrosol LR: 2.0 g; Nitrosol GR: 2.0 g; Aq. PVA solution (7.4 w/v%): 108.0 g; Aq. APS solution (6.5 w/v%): 21.4 g; Aq. SMS solution (6.5 w/v%): 21.4 g; distilled water: 60.0 g

Nitrogen pressure was kept higher than the pressure in the reactor to ensure complete transfer of solution. This led to an increase in pressure by 50 psi. After 30 min 25 mL VAc, 4 mL APS sol and 4 mL SMS solution were charged into the reactor as described earlier, thereby leading to a further increase in pressure. Ethylene (50 psi) was fed into the reactor after 30 min followed by 25 mL VAc, 4 mL APS and 4 mL SMS. Same procedure was repeated two more times and then the reaction was allowed to run for 3 h at 40°C.

Results and discussion

Gel content and solid content of vinyl acetate– ethylene copolymers as well as poly(vinyl acetate) prepared by emulsion polymerisation are shown in the Table 2. The percent solid content of the latex was only marginally affected by increasing the ethylene pressure. Gel content was higher in poly(vinyl acetate) than its copolymers with ethylene. An increase in ethylene pressure or increase in cyclohexane content resulted in a decrease in gel content. Gelation in vinyl acetate – ethylene copolymer systems occur by the transfer of hydrogen atom from acetate methyl group to another growing polymer chain as shown in Eq. (1).



$$-(CH_2CH_2)_n-(CH_2\underset{\underset{\underset{CH_3}{|}}{\underset{C=O}{\underset{|}{O}}}}{\underset{|}{CH}})- + P^{\bullet} \longrightarrow -(CH_2CH_2)_n-(CH_2\underset{\underset{\underset{\overset{}{CH_2^{\bullet}}}{|}}{\underset{C=O}{\underset{|}{O}}}}{\underset{|}{CH}})- + PH \qquad (1)$$

The C–H bond of the acetate methyl group is weakened by the electron withdrawing character of the adjacent carbonyl group. The radical produced is thus resonance stabilised and propagation can occur resulting in long acetate branches thereby increasing the M_w and finally leading to gelation.

Table 2 Gel content and solid content of vinyl acetate–ethylene copolymers

No.	Sample designation	Gel content/%	Solid content/%
1.	714	7.8	35.5
2.	716	6.8	34.3
3.	723	9.1	34.2
4.	724	10.5	32.9
5.	908	>15.0	35.7

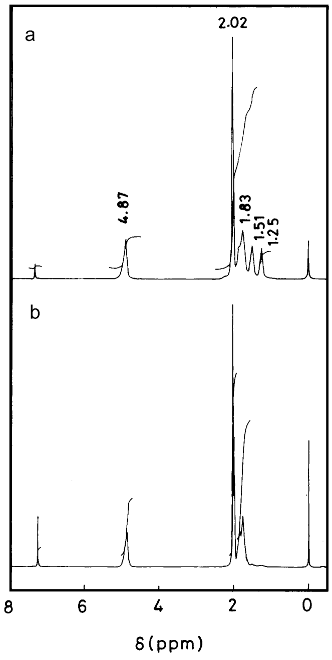


Fig. 1 ^{1}H-NMR of (a) sample 714 and (b) sample 908

Copolymer composition (wt% ethylene) of vinyl acetate–ethylene copolymers was determined by recording the ^{1}H-NMR spectra of the samples obtained after removing the gel portion. In the ^{1}H-NMR spectrum of poly(vinyl acetate) characteristic proton resonance signals due to methylene, methyl and methine protons were observed at 1.76, 2.02 and 4.87 ppm respectively (Fig. 1(b)). The positions of these proton resonance signals did not change by introduction of ethylene in the backbone (Fig. 1(a)). However, additional resonance signals due to ethylene protons were observed at 1.25 and 1.5 ppm. In EVA copolymers containing 6 to 20 mol% of vinyl acetate, the acetate methyl, methylene and methine protons have been reported at 1.7, 1.2 and 5.0 ppm [12].

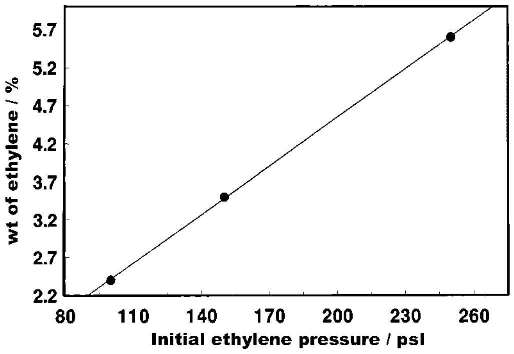


Fig. 2 Effect of initial pressure of ethylene on composition of VAE copolymers

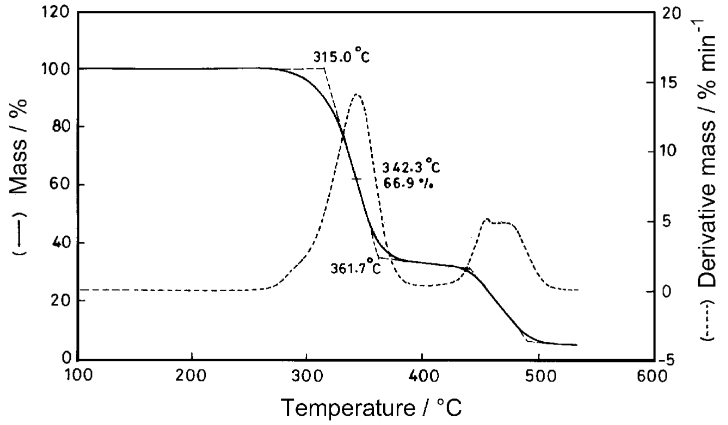


Fig. 3 TG trace of sample 714

The copolymer composition was determined by taking ratio of peak areas of methyl prolons (2.02 ppm) and ethylene protons (1.5 and 1.25 ppm). The copolymers prepared by using high initial ethylene pressures were found to contain high ethylene content (Fig. 2). Increase in cyclohexane concentration did not affect the

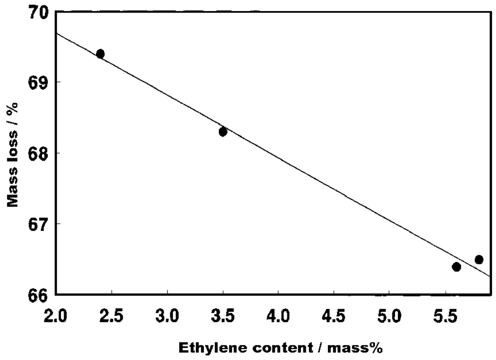
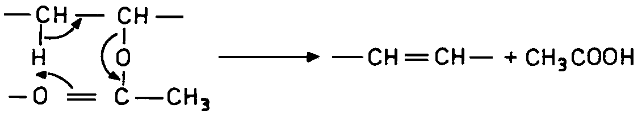


Fig. 4 Effect of copolymer composition on thermal degradation (temperature range – 250–350°C) of VAE copolymers in nitrogen atmosphere

ethylene content of copolymers (sample 714 and 716 which were found to be 5.6 and 5.8 wt% respectively).

In the TG traces recorded in nitrogen atmosphere, a two-step decomposition was observed (Fig. 3). The copolymers were stable upto 250°C and started loosing mass above this temperature. In the first step in the temperature range of 250–350°C, acetic acid from vinyl acetate is eliminated via six-membered transition state as shown in Eq. (2). The observed mass loss in second step (temperature range – 350–450°C) is due to fragmentation and break down of polymer backbone.



(2)

The mass loss in first step was noted down from the TG traces of different copolymer samples. A plot of mass loss *vs.* ethylene content of copolymers was found to be linear indicating thereby a good correlation between thermal degradation of copolymers and vinyl acetate/ethylene content. Thus TG offers a convenient method for elucidating composition of VAE copolymers.

* * *

The Ministry of Human Resource Development, Govt. of India and HMG Industries Ltd. are gratefully acknowledged for providing financial assistance to carry out this collaborative research project.

References

1 P. I. Scott, A. Penlidis and G. L. Rempel, J. Polym. Sci., 31 (1993) 403.
2 P. I. Scott, A. Penlidis and G. L. Rempel, J. Polym. Sci., 31 (1993) 2205.
3 R. J. Koopmans, R. V. Der Linden and E. F. Vansant, Polym. Engg. and Sci., 22 (1982) 878.

4 D. Munteanu, Rev. Chem. (Bucharest), 27 (1976) 902.
5 J. Mayor and J. Sodomka, Vyzkumny Makromol. Chem. (Brno), 26 (1975) 601.
6 E. M. Barrall II, R.S. Porter and J. F. Johnson, Anal. Chem., 35 (1963) 73.
7 J. Chiu, Appl. Polym. Symp., 2 (1966) 25.
8 J. Chiu, Anal. Chem., 40 (1968) 1516.
9 A. Streitwieser and C.H. Heathcock, 'Introduction to Organic Chemistry', P.15, Mcgraw-Hill, 3rd ed. (1976).
10 V. Barboiu, A. Natansohn, C. Andrei and D. Blum, Rev. Roum. Chim., 25 (1980) 993.
11 Y. Yawaka, T. Tsuchihara, N. Tanaka, K. Kosaka, Y. Hirakida and M. Ogawa, Kobunshi Kagaku, 28 (1971) 459.
12 T. K. Wu, J. Polym. Sci., A-2 (1970) 167.
13 F. Keller and H. Roth, Plast. Kaut., 15 (1968) 80.
14 J. Schaefer, J. Phys. Chem., 70 (1966) 1975.