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INHIBITION OF BULK POLYMERIZATION OF VINYL ACETATE IN THE PRESENCE OF CASTOR OIL PREPOLYMER (COP)

A.H.K. Yusufzai and A. Rasheed Khan

PCSIR Laboratories, Karachi, Pakistan

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The bulk polymerization of vinyl acetate was inhibited in the presence of small amounts of Castor Oil Prepolymer (COP). Polymerization were carried out at 25° using benzoyl peroxide as a catalyst and dimethyl aniline as promotor. A plot of induction period VS concentration of COP and the usual polymerization curves in presence of COP is reported. A possible explanation has been given.

INTRODUCTION

The bulk polymerization of vinyl acetate has been studied in detail by a number of workers [1–4]. It was noted as early as 1958 by Stockmeyer *et al.* [5] that traces of residual impurities such as ethylene diacetate and ethylidine diacetate can suppress the rate of polymerization. Later on Burnett and loan [6] found that presence of a small amount of benzene reduces the rate to half the rate of bulk polymerization of vinyl acetate at 60°. They also found that the rate drops rapidly with decreasing monomer concentration. Further more they found that the radicals formed with the transfer of solvent was relatively unreactive. Bengough *et al* [7] also reported the inhibition of radical polymerization of vinyl acetate in the presence of small amounts of inorganic salts.

Recently, we have prepared a synthetic rubber from castor oil prepolymer [8]. In an attempt to improve its properties COP has been found to copolymerize with a number of vinyl monomers. Good yields of copolymers were obtained with acryonitrile. However, when attempts were made to copolymerize COP with vinyl acetate, the results were surprising as it did not form any copolymer with vinyl acetate but inhibited the polymerization of vinyl acetate in small amounts. The present paper deals with the inhibition of polymerization of vinyl acetate with COP.

EXPERIMENTAL

Materials

1. Vinyl acetate (E. Merk) was purified by distillation on a long column and the fraction boiling at 72–73° was collected.
2. Caster oil prepolymer (COP) was prepared according to the procedure stated else where [8].
3. Benzoyl peroxide of reagent grade was twice recrystallised in chloroform.
4. Dimethyl aniline of E. Merck was used without further purification.
5. Reagent grade methanol and acetone were distilled before use.

Procedure

All polymerization reactions were carried out in dilatometers consisting a cell of 5 ml capacity and a capillary 23 cm in length and 0.15 cm of diameter. 5 ml of vinyl acetate and 5g per litre benzoyl peroxide was added to the dilatometer. A known quantity of COP was added to each reaction tube. The dilatometer, was kept in ice cooled water. The reaction was started after keeping the dialatometer at 25° in a thermostatically controlled bath by adding dimethyl aniline (0.009 g) into the cell as promoter. After the incubation period the monomer begins to polymerize resulting in fall of the meniscus level. After each small interval of time, the change in meniscus level was noted. Rate of polymerization was calculated from change of meniscus in dilatometer.

DISCUSSION

Effects of castor oil prepolymer (COP) on the bulk polymerization of vinyl acetate are summarized in Table 1. Contrary to our expectation COP and vinyl acetate did not form a copolymer; on the other hand bulk polymerization of vinyl acetate was very much retarted in the presence of small amounts of COP. Fig.1 shows the polymerization

Table 1. Inhibition effect of COP on vinyl acetate polymerization

Vinyl acetate ml	COP %	Induction period (min)	Rate of polymerization mole/1/sec.
5.00	0.00	35	3.06700×10^{-4}
5.00	0.20	70	1.68285×10^{-4}
5.00	0.40	80	1.55208×10^{-4}
5.00	0.60	105	1.21352×10^{-4}
5.00	0.80	125	1.13617×10^{-4}

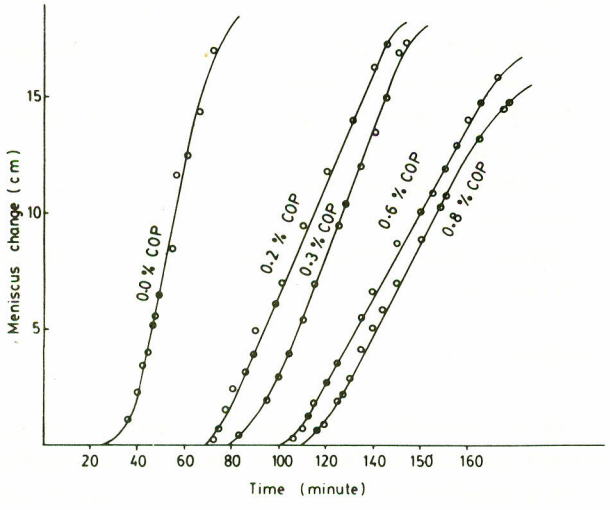

Fig. 1. Effect of varying amounts of COP on polymerisation.

curves in presence of COP. Increase in the concentration of COP normally increases the induction period. (Fig.2) The polymerization of vinyl acetate take place in almost the same rate.

It has already been reported that COP forms low molecular weight copolymer with acrylonitrile [9]. It appears that small amount of COP in the presence of vinyl acetate is consuming the initiating radicals formed by the decomposition of benzoyl peroxide in presence of dimethyl aniline, thus preventing the vinyl acetate bulk polymerization. As indicated from Fig.1 the induction period increases with the concentration of COP. It is evident from Fig.1 that after long induction period the rate of polymerization of vinyl acetate is also lowered. This is because of the probable

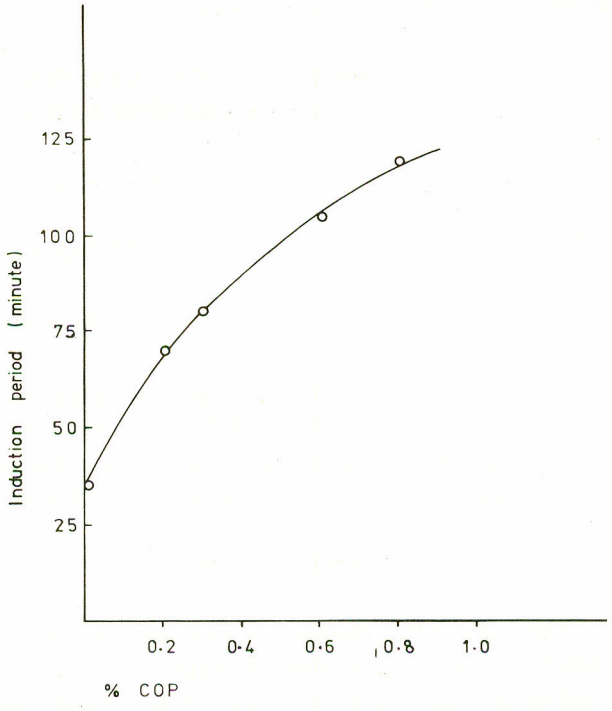

Fig. 2. Effect of varying amounts of COP on the induction period.

polymerizability of COP itself. The plot of time against meniscus change (Fig.1) also suggests that COP inhibits bulk polymerization of vinyl acetate.

REFERENCES

1. G.H. Burnett and H.W. Melville, Proc. R. Soc. London, **A–189**, 456,481,495 (1947).
2. S. Kamerskya and S.S. Medvedev Acta Physicochim USSR, **13**, 565 (1940)
3. P.W. Allem. E.M. Merrett and J. Scamlan, Trans. Faraday Soc., **5**, 95 (1955).
4. A.C. Cuther Son, G. Gee and Rideal Proc. Soc. London, **A–170**, 300 (1939).
5. W.H. Stockmayer and Reebles, J. Am. Chem. Soc. **75**, 2278 (1953).
6. G.M. Burnett and L.D. Loan. Trans faraday Soc.,**51**, 219, (1955).
7. W.I. Bangouh and W.H. Fairservice, Trans. Faraday Soc., **3**, 382 (1967).
8. Patent applied for
9. A.H.K. Yousufzai, A. Rasheed Khan, H. Imam and Farooqui, J. Macro Molecular Science – chemistry, **A17** (3), 381–385 (1982).