

Curing Reactions in Plastic Prepolymers and Propellants. I. Polystyrene

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Synopsis

Curing reactions of the viscous PS prepolymer and PS/AP propellant slurry have been studied. The molecular weight of the binder (separated from the propellant) and the prepolymer was found to increase to a maximum value, remain constant for some time, and then fall off between 50–125°C. The molecular weight of the binder was found to be less than corresponding prepolymer between 100–150°C but at lower temperatures (50–75°C) the reverse was found to be true. The increase in the molecular weight during curing at lower temperatures has been explained on the basis of Trommsdorff effect which gets support from the estimated activation energy (9 kcal mole⁻¹) for the curing process. Curing was recognized as chain extension where the rate of polymerization becomes diffusion controlled below 75° C.

INTRODUCTION

Curing is done to achieve desired mechanical properties of a viscous prepolymer or composite solid propellant mix. A thorough understanding of the curing reactions in prepolymers, particularly in composite solid propellants, is of immense importance for getting reliable and desirable mechanical properties. Generally the elastomeric polymers like carboxy-terminated polybutadiene, hydroxy-terminated polybutadiene, polyesters, polyurethanes, etc., and the propellants based on them are cured through a chemical process by the addition of crosslinking agents¹ to achieve a three-dimensional network. On the other hand, in plastic prepolymers and propellants based on these plastic polymers, the curing process is a physical one in which the viscosity of the matrix and solid increases to the point where the flow disappears, and curing is achieved by applying thermal energy without the aid of crosslinking agents. Whereas some attempts have been made^{1–3} in the past to understand the curing reactions of elastomers where crosslinking agents are used, a systematic study of the physical curing of prepolymers or prepolymer in solid propellant slurry has not yet been done. The purpose of the present work is to understand the physicochemical changes occurring during the curing of plastic prepolymers and plastic propellants. A typical prepolymer, polystyrene (PS), and corresponding polystyrene/ammonium perchlorate (PS/AP) propellant slurry have been chosen for detailed study. It may be mentioned that this study is also intended to reveal the effect of nonreinforcing filler AP on the curing process of PS.

EXPERIMENTAL

Viscous prepolymer was prepared from fractionally distilled styrene by heating it at 50°C for 24 hr with 1% benzoyl peroxide initiator.⁴ The propellant mix containing 25% viscous PS and 75% AP (particle size 53–151 μm) was filled in several soft glass test tubes and kept at 50, 75, 100, 125, and 150°C in air for curing. Samples were taken out at different intervals of time and extracted with benzene to dissolve the polymer part, followed by filtering through a G3 sintered crucible. PS was precipitated from benzene extract by adding excess methanol and dried under vacuum at room temperature. The precipitated PS thus obtained from the propellant will henceforth be called the binder. Controls involving the viscous PS prepolymer in the absence of AP were also kept for curing in air. PS samples in the absence of AP will, for convenience, be called the prepolymer. Viscosity measurements using a Ubbelohde dilution viscometer were carried out for all the binder and prepolymer samples at 30°C using benzene as solvent. Similar experiments for curing at 150°C in N_2 atmosphere were also done with PS, PS/AP, and PS/NaCl. No gel formation was observed in any of the systems investigated.

RESULTS AND DISCUSSION

The viscosity data in benzene were used to calculate the reduced specific viscosity $\eta_{sp/c}$, inherent viscosity η_{inh} , and the intrinsic viscosity $[\eta]$ was derived from them. The viscosity average molecular weight (M_v) was calculated⁵ by using the Mark-Houwink equation, $[\eta] = 0.85 \times 10^{-4} M_v^{0.75}$. The time versus molecular weight results have been plotted for each temperature and are presented together in Figures 1 and 2. Figure 1 shows that the molecular weight of binder and prepolymer first increases to a maximum value, remains constant for some time, and then falls off at all the four temperatures 50, 75, 100, and 125°C, but not at 150°C. The increase in molecular weight is more pronounced at 50°C than at 75, 100, and 125°C. At 150°C the molecular weight falls off rapidly, remains stationary up to 50 hr, and then starts falling off again.

From Figure 2 it is clear that the molecular weight of the binder is less than that of the prepolymer for temperatures 100, 125, and 150°C. But at 50 and 75°C the molecular weight of the prepolymer is less than that of the binder at the initial stages. The difference between the molecular weight of the binder and that of the prepolymer is initially less but increases as the curing period is increased. The increase in molecular weight during curing at lower temperatures may be attributed to the acceleration of polymerization due to the retardation of the termination step owing to the high viscosity of the polymer matrix, i.e., the natural mobility of the polymeric radicals is so hindered that the probability that the two radicals will meet and terminate is greatly reduced.⁶ The decrease in molecular weight of the binder at high temperature may be due to the oxidation by the air adsorbed or to the products of AP decomposition.⁷⁻⁹ To clarify this, (1) PS prepolymer alone, (2) in the presence of AP, and (3) in the presence of sodium chloride was cured at 150°C in nitrogen atmosphere. The results are presented in Figures 3 and 4. It was observed that the sample containing AP after curing turned yellow homogeneously throughout the bulk of the material, while the sample containing sodium chloride, as well as the prepolymer sample itself, was colorless. In Figure 3 the rapid decrease in molecular weight

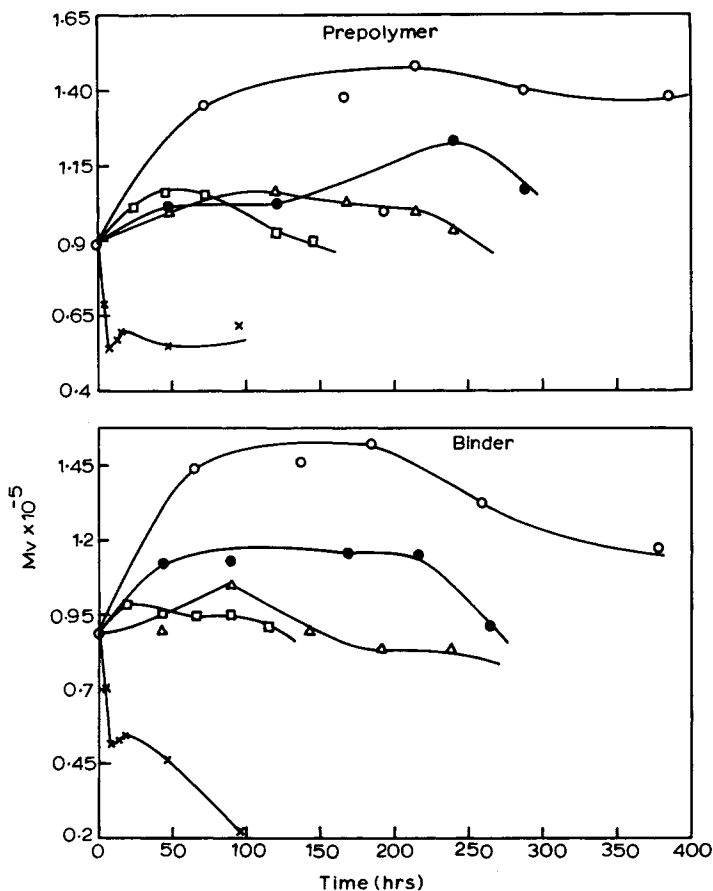


Fig. 1. Change of viscosity-average molecular weight with time for prepolymer and binder in air at different temperatures ($^{\circ}\text{C}$): 50 (O), 75 (■), 100 (■), 125 (□), and 150 (×).

of the PS in the PS/AP sample alone indicates the degradation of PS in presence of AP. The infrared spectra of the binder sample cured at 150°C in air and nitrogen atmosphere (Fig. 4) show the presence of carbonyl peak around 1700 cm^{-1} . The absence of this peak in PS extracted from dummy propellant (PS/NaCl) and prepolymer alone indicates the oxidative degradation of PS and PS/AP propellant. Thus the degradation of the binder at higher temperatures is mainly due to the presence of AP, which promotes oxidative attack on the binder. This could explain the decrease in the molecular weight of the binder compared to the corresponding molecular weight of the prepolymer.

A cursory look at Figures 1 and 2 indicates that the nature of the curing reactions, in general, are similar for both the prepolymer and binder; the actual rate may, however, be different in the two cases. In order to examine quantitatively whether the nature of the curing reactions for both the binder and prepolymer is the same, activation energy (E) calculations were carried out in the temperature range $50\text{--}100^{\circ}\text{C}$. Arrhenius plots were obtained by plotting the logarithm of the curing rate (inverse of time taken to reach the molecular weight 0.975×10^5) versus the inverse of the temperature [Fig. 5(A)]. The E value for the curing process of both binder and prepolymer was found to be 9 kcal mol^{-1} . A closer

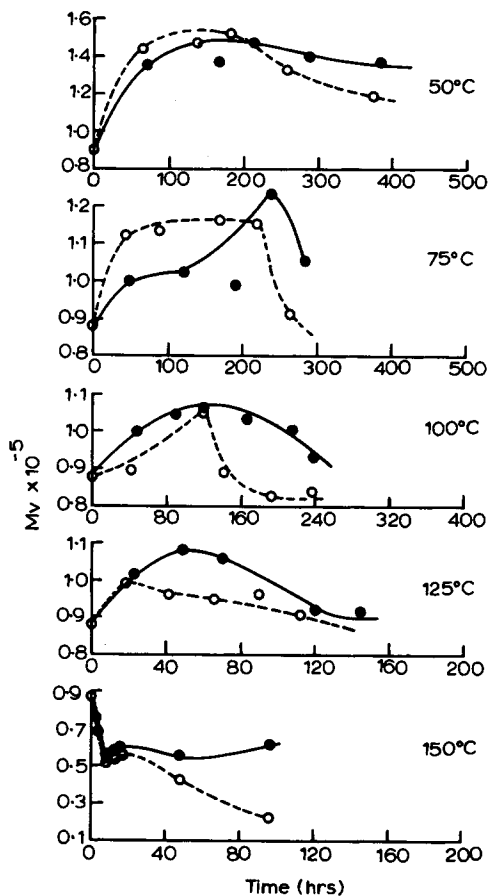


Fig. 2. Comparison of the dependence of viscosity-average molecular weight on curing time for binder (O) and prepolymer (□) at different temperatures in air.

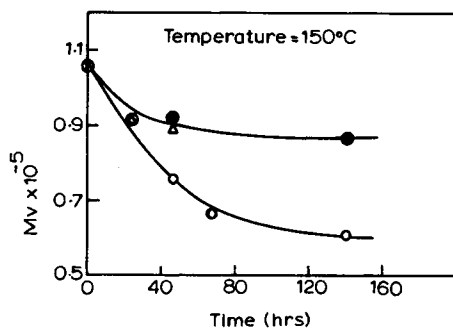


Fig. 3. Change of molecular weight with time for PS prepolymer (Δ), PS in PS/AP (O), and PS in PS/NaCl (\otimes) at 150°C in nitrogen atmosphere.

analysis of Figure 5(A), however, shows that the activation energy below 75°C is much lower than 9 kcal mol⁻¹, confirming the Trommsdorff effect.⁶ This suggests that the curing process may be recognized as a chain extension, where the rate of polymerization becomes diffusion controlled below 75°C.¹⁰

The fact that the rate-controlling process during the curing of a plastic pre-

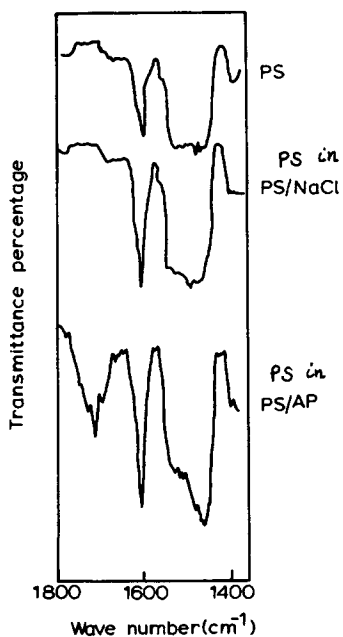


Fig 4. Infrared spectra of PS, PS in PS/AP, and PS in PS/NaCl cured at 150°C in nitrogen atmosphere in benzene.

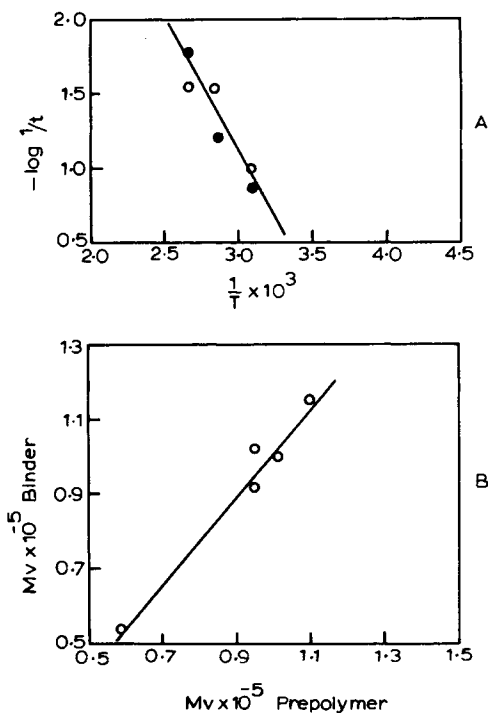


Fig. 5. (A) Arrhenius plot for the curing of prepolymer (O) and binder (●) in the range 50–100°C. (B) Dependence of molecular weight of the binder and prepolymer at different temperature for a 25-hr curing time.

polymer is not affected by reactive oxidizer like AP is confirmed from the Figure 5(B), where the molecular weight for the binder at 25 hr at different temperatures is plotted against the corresponding molecular weight of the prepolymer. A linear dependence is obtained, showing that the data fall on a single master curve independent of curing temperature. This also suggests that the curing process of the propellant has a relation to the curing process of prepolymer.

Recent work by Kishore et al.¹¹ has shown that the mechanical properties of the propellant are linearly dependent on the molecular weight of the polymer. This suggests that the curing of the propellant at 50°C would yield the best mechanical properties, as compared with curing at higher temperatures, since the molecular weight of the propellant cured at 50°C is higher than that obtained by curing at higher temperatures. Thus PS/AP propellant curing should be carried out at 50°C for 10 days to achieve optimum properties.

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