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The interaction between PTFE and porous metals and metal blacks - rheological characterization and thermal degradation of the polymer

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High molecular weight PTFE ($\bar{M}_n = 10^4$ to 10^6) normally exhibits high thermal stability and melt viscosity. When contacted by high surface area metal blacks (Au or Pt) or porous sintered metals (Au or Ni) and heated near the melting temperature, the effective viscosities and thermal stabilities of the PTFE are orders of magnitude lower than those normally exhibited by the polymer. These results are discussed in terms of capillary flow, heterogeneous catalytic degradation, and the diffusion controlled evolution of volatile decomposition products.

1. Introduction

Some molten polymeric materials are characterized by low surface tension values and tend to adhere strongly to so-called high energy surfaces such as those of metals and metal oxides [1–3]. The rate at which a molten polymer will spread upon a high surface energy material will, in general, decrease with increasing melt viscosity [3]. Since the viscosity of high molecular weight PTFE in the vicinity of the melt temperature (330 to 350° C) has been reported to be between 10^{10} and 10^{12} P, good interfacial contact between molten PTFE and porous metal or metal oxide surfaces should be achievable only after very long periods of heating [4–6].

In addition to the high melt viscosity, high molecular weight PTFE is commonly considered to have the highest resistance to thermal degradation of any synthetic polymer in general use. This is one of the most important characteristics of high molecular weight PTFE so far as its technological usefulness is concerned. Gravimetric analysis is the usual method used to detect PTFE degradation, and the gases given off have been found to contain at least 95% monomer [5]. Although there is mass spectrometric evidence to show that PTFE degradation begins at temperatures as low as 300° C [7, 8], gravimetric methods have generally not been useful at temperatures below 360° C, and appreciable rates of weight loss are not seen below 425° C (0.1% per hour) [5]. Above this temperature, the weight loss data have yielded a pre-exponential factor of about 10^{19} sec^{-1} and an activation energy of about 81 kcal mol^{-1} for PTFE decomposition in vacuo [9, 10]. In this temperature range, the decomposition has been shown to be independent of molecular weight over a range from 5×10^5 to 10^7 [10]. The extrapolated rate for vacuum decomposition is about 3×10^{-6}% per min at 350° C.

In the work reported here, we have examined the rheological behaviour of the PTFE as well as the thermal degradation that occurs when thin layers of high molecular weight PTFE are heated in the vicinity of the melt temperature while in contact with porous metals and metal blacks. The results are not at all those that would be expected based upon the reported viscosities and thermal stabilities of bulk PTFE.

2. Experimental

Two finely divided PTFE materials were used with average molecular weights of approximately 6×10^4 and 5×10^6. Layers of these two materials (with 6 cm^2 geometric surface areas and containing between 1 and 2 mg of PTFE per cm^2) were prepared by filtration of aqueous or alcoholic dispersions upon sheets of porous nickel or gold. The porous metal substrates were prepared by the high temperature sintering of pressed layers of the metal powders and were approximately 50% porous with pore diameters ranging up to a few microns. In some instances, a layer of gold or platinum black (1 mg cm^{-2}) was formed subsequently by filtration from an alcoholic dispersion in such a way that the metal black and PTFE layers overlapped. All samples (contained within aluminium foil pans) were then heated in an air filled convection oven at 335 to 337° C.

Two series of measurements were performed on the samples containing only a layer of PTFE deposited upon the porous sintered metal substrate. The thermal degradation of the PTFE was monitored as a function of time at temperature by periodically weighing the samples using a Mettler analytical balance. When porous nickel (rather than porous gold) substrates were used, they were heated in the air at 335 to 337° C until the rate of weight gain due to nickel oxidation reached a small and constant value before the PTFE layer was deposited by filtration. For purposes of comparison, weight loss measurements were performed simultaneously upon two other samples consisting of pieces of smooth gold foil upon which about 8 mg of PTFE were deposited. These two samples were heated in the same oven as were the samples of PTFE deposited upon the porous sintered metal substrates.

Penetration of the PTFE into the pores of the metal substrates was also examined as a function of time at temperature using conventional optical microscopy as well as with the use of a JEOL JXA-50A electron probe microanalyser. The cross-sectioned samples were prepared for examination by mounting in epoxy, grinding, and polishing. A thin film of carbon was deposited by evaporation upon the surface of each polished sample to establish electrical continuity. The distribution of PTFE within each sample was determined by the X-ray mapping technique using the $FK\alpha$ wavelength.

Water wettability was used as a probe to monitor the penetration of the PTFE into an overlapping gold black or platinum black layer as a function of time at temperature (see Fig. 1a). Small droplets of distilled water were placed at various points upon the metal black layer. Before the sample was heated, the entire metal black layer was always completely wettable. After a few minutes of heating, however, that portion of the metal black layer which overlapped the PTFE layer was no longer water wettable. With further heating, a band of non-wettable metal black was observed to advance from the original PTFE/metal black interface (see Fig. 1b). The width of this wetproofed band of material increased with time at temperature and was determined by the use of a microscope-camera assembly. Chemical analysis of the wetproofed portion of the metal black layer indicated the presence of a fluorine-containing material.

The scanning electron microscope was also used to investigate the penetration of PTFE (average molecular weight 5 x 10^6) into an overlapping gold

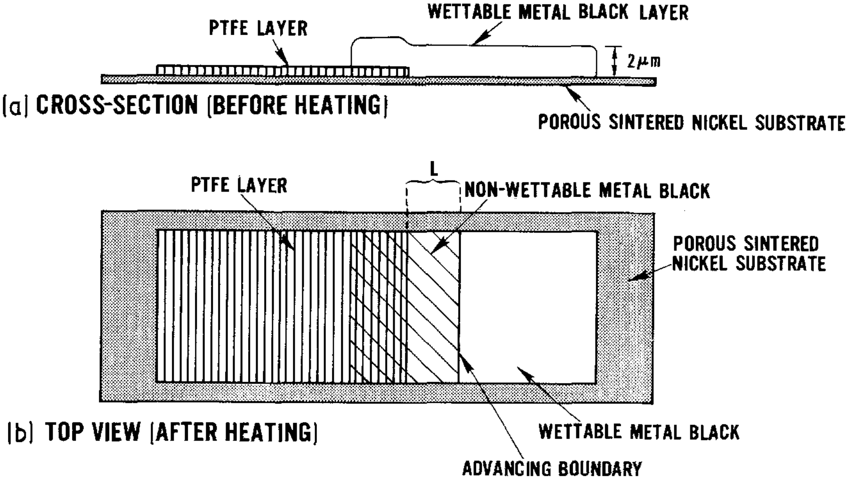

Figure 1 Schematic diagram of sample configuration: overlapping layers of PTFE and metal blacks.

black layer. After heating in the air at 335 to 337° C for about 50 h, the sample was exposed to hot (80° C) aqua regia for successive 5 sec time intervals. After each exposure to the concentrated acid solution, a portion of the sample was removed for later microscopic examination. To facilitate the scanning electron microscopic analysis, the cleaned and dried samples were sputter coated with a 100 Å layer of platinum.

3. Results and discussion

Experimental data for the penetration of two high molecular weight PTFE materials (average molecular weights of 6×10^4 and 5×10^6) into contacting layers of sintered porous gold and oxide-covered nickel at 335 to 337° C are shown in Fig. 2. The maximum distance of penetration has been plotted versus the square root of the time at temperature and it is seen that linear relationships are obtained. In particular, after one hour at 335 to 337° C, the PTFE materials have penetrated about 15 μm into the pores of the sintered gold substrates.

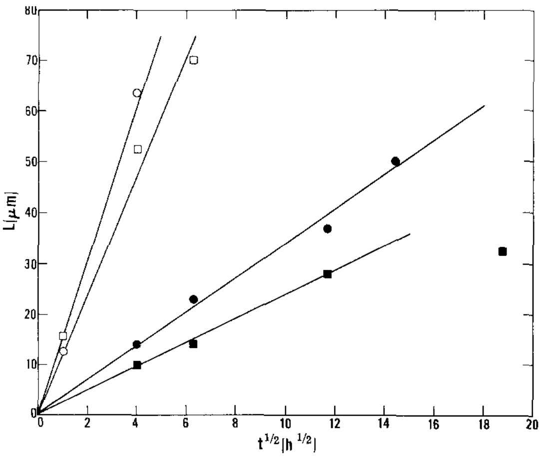

Figure 2 PTFE penetration into porous metal substrates at 335 to 337° C: F$K\alpha$ X-ray mapping data. (○) $\bar{M}_n \approx 6 \times 10^4$, on porous Au; (●) $\bar{M}_n \approx 5 \times 10^6$, on porous Au; (□) $M_n \approx 6 \times 10^4$, on porous Ni; (■) $\bar{M}_n \approx 5 \times 10^6$, on porous Ni.

Owing to the observed linear relationships, it is tempting to apply the Washburn equation for capillary flow, Equation 1, in order to calculate the apparent viscosities of the two PTFE samples.

$$x^2 = \frac{\gamma \cos\theta \, r \, t}{2\eta}. \qquad (1)$$

In this equation, x is the distance of penetration in time t, γ is the PTFE surface tension (taken to be 20 dyn cm^{-1}), η is the viscosity, r the pore radius (0.5 to 2.5 μm for the porous sintered gold and nickel), and θ the contact angle (assumed to be 0°). Using these values, the data yield calculated viscosities of (1 to 5) $\times 10^6$ P for the 6×10^4 average molecular weight PTFE sample and (2 to 10) $\times 10^7$ P for the 5×10^6 average molecular weight material, values several orders of magnitude smaller than the commonly accepted viscosity range.

The data shown in Fig. 2 were obtained using the electron microprobe X-ray mapping technique. It should, however, be noted that with conventional optical microscopy using standard metallurgical techniques, it was difficult to detect the presence of the PTFE within the pores of the highly reflective gold and nickel substrate layers. Nevertheless, penetration of the PTFE into the porous sintered metal sheets could always be inferred from the disappearance of the PTFE from the external surfaces of the porous substrates.

In view of the anomalously low effective viscosities of high molecular weight PTFE materials heated near the melting temperature while contacting porous gold and oxide covered nickel substrates, the thermal stabilities of these PTFE materials were examined under the same experimental conditions. For purposes of comparison, the thermal stabilities of the 6×10^4 and 5×10^6 average molecular weight polymers were also determined with the use of smooth gold foil substrates in place of the porous ones.

All of the experimental results are plotted in Fig. 3 as percentage volatilization versus time at 335 to 337° C. The 6×10^4 and 5×10^6 average molecular weight PTFE samples supported on the smooth gold foil substrates lost about 2% and 0.5% of their total initial sample weights, respectively, after about 700 h at temperature. Furthermore, the entire observed weight losses for these samples occurred in about the first 300 h of heating suggesting that the volatilization of low molecular weight impurities initially present in the samples might have been responsible for the bulk of the measured weight losses.

In contrast, the 6×10^4 and 5×10^6 average molecular weight PTFE samples supported on the porous sintered gold substrates lost about 31% and 19% of their initial sample weights, respectively, during 700 h of heating. Thus, these high molecular weight PTFE materials supported upon porous gold substrates volatilize between one and two orders of magnitude faster, at 335 to 337° C, than do the same PTFE materials heated at 335 to

337° C while contacting the porous gold substrates. Similarly, the volatilities of the PTFE materials heated at 335 to 337° C while contacting the porous gold substrates are between one and two orders of magnitude greater than those predicted by extrapolation of higher temperature data for comparable materials reported by other investigators [9].

As shown in Fig. 3, the data obtained using porous oxide covered nickel substrates indicate even lower thermal stabilities under these conditions for the two PTFE materials examined. Specifically, in about 650 h at 335 to 337° C the 6×10^4 and 5×10^6 average molecular weight samples had lost about 83% and 60% of their initial sample weights, respectively, assuming constant substrate weights. The porous sintered nickel substrates were preheated in the air at the experimental temperature until the rate of weight gain due to nickel oxidation had reached a small and constant value prior to the deposition of the PTFE materials. While the rates of substrate weight gain or loss subsequent to contacting the PTFE are not known, they are expected to be small. Nevertheless, the volatilization rates indicated in Fig. 3 for the samples containing porous nickel substrates are not as reliable as those obtained using the gold substrates.

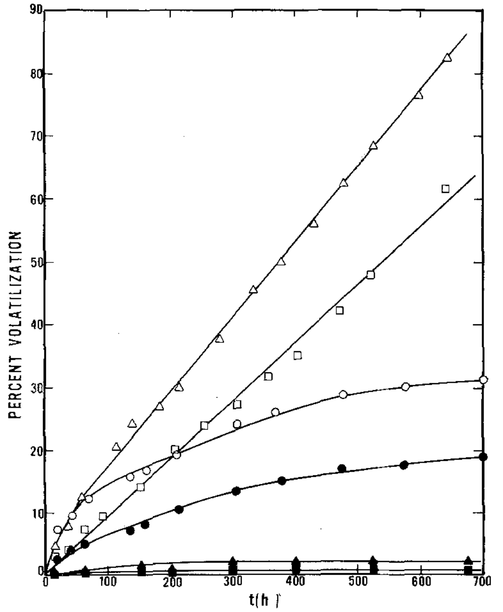

Figure 3 Volatilization of PTFE contacting metal substrates at 335 to 337° C. (●) 7.4 mg, $\bar{M}_n \approx 5 \times 10^6$, on porous Au; (○) 8.3 mg, $\bar{M}_n \approx 6 \times 10^4$, on porous Au; (□) 7.6 mg, $\bar{M}_n \approx 5 \times 10^6$, on porous preoxidized Ni; (△) 8.1 mg, $\bar{M}_n \approx 6 \times 10^4$, on porous preoxidized Ni; (■) 8.6 mg, $\bar{M}_n \approx 5 \times 10^6$, on smooth Au; (▲) 7.6 mg, $\bar{M}_n \approx 6 \times 10^4$, on smooth Au.

Taken as a whole, these results indicate that, when high molecular weight PTFE materials are heated in the vicinity of the melt temperature while contacting porous metal and oxide covered metal substrates, the effective viscosities and thermal stabilities of the PTFE are orders of magnitude smaller than those characteristic of PTFE heated at the same temperatures but not in contact with such porous materials. The results also indicate that, the lower the average molecular weight of the PTFE, the lower the effective viscosity and thermal stability.

Similar rheological characteristics have also been found for PTFE heated near the melt temperature while in contact with layers of gold and platinum black. As mentioned previously, the experimental configuration consisted of overlapping layers of PTFE and metal black, both supported upon a porous nickel substrate. Before heating, the metal black was always found to be water wettable as shown in Fig. 1a. After a short period of heating in the air at 335 to 337° C, the portion of the metal black layer which overlapped the PTFE layer was found to be non-wettable. With further heating, a band of wetproofed metal black was found to advance from the original PTFE/metal black interface as shown in Fig. 1b. This wetproofed band of material was shown by chemical analysis to contain fluorine-containing materials. The width, L, of the wetproofed band of metal black has been plotted in Fig. 4 versus the square root of the time at temperature for overlapping structures of gold black or platinum black with the 6×10^4 average molecular weight PTFE material, and for an overlapping structure of gold black with the 5×10^6 average molecular weight PTFE. As in the case of PTFE penetration into the sintered porous gold and oxide covered nickel substrates, the greatest distance of penetration, assumed to be at least proportional to the width of the wetproofed band of metal black, increases approximately linearly with the square root of the time at temperature.

The scanning electron microscope revealed that a honeycomb network of thin PTFE films remains after the dissolution of the wetproofed gold black in hot aqua regia. In Fig. 5 are shown typical high resolution electron micrographs of the surface of this porous PTFE structure at a point about 4 mm

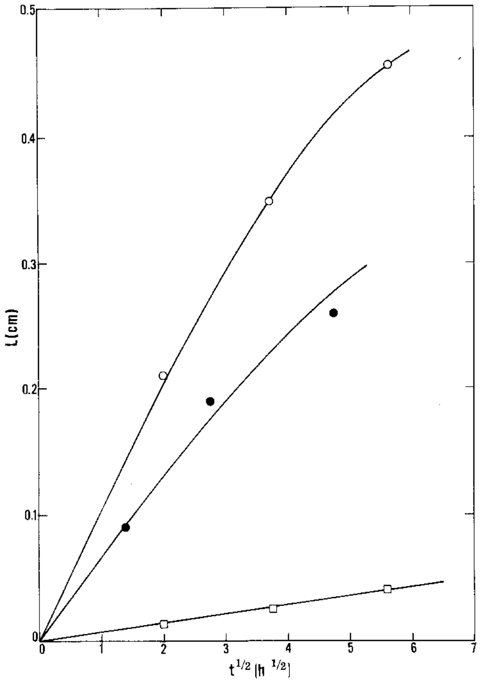

Figure 4 PTFE penetration into overlapping metal black layers at 335 to 337° C: water wettability data. (○) $\bar{M}_n \approx 6 \times 10^4$, Au black; (●) $\bar{M}_n \approx 5 \times 10^6$, Au black; (□) $\bar{M}_n \approx 6 \times 10^4$, Pt black.

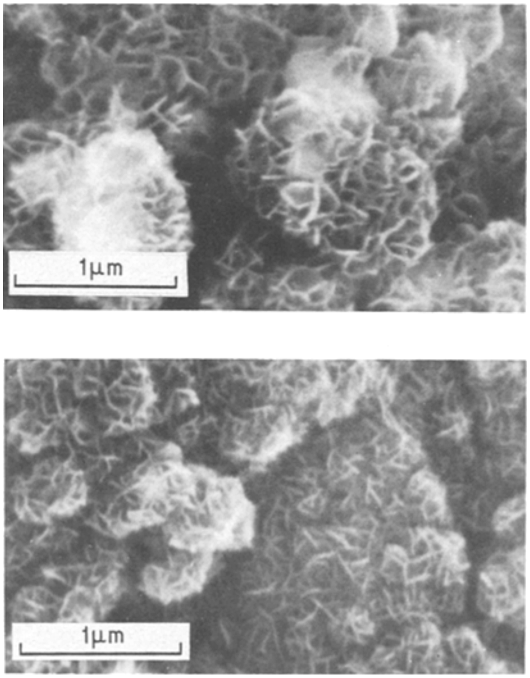

Figure 5 High resolution electron micrographs of the porous PTFE structure remaining after dissolution of the wetproofed gold black.

from the original PTFE/gold black interface. The apparent thicknesses of the PTFE films are on the order of 100 Å. The actual thicknesses are certainly considerably smaller since, to prevent electrical charging effects during electron microscopic examination, the samples were coated with a layer of platinum which was itself about 100 Å thick. The cells formed by these thin PTFE films are about 500 to 1000 Å across, roughly the size of the gold black particles which presumably resided within these cells before being removed with the hot aqua regia.

Of the possible causes of the very high rates of thermal decomposition observed for PTFE heated in the vicinity of the melt temperature while contacting porous sintered metals and oxide covered metals, two seem most probable. First, as a result of the high metal/PTFE interfacial contact area achievable within the sintered porous metal substrate, catalytic effects from the metal surface acting upon the degradation of the PTFE can become important. In cases where only relatively low metal/PTFE interfacial areas are encountered (e.g. when the PTFE is heated while contacting smooth metal foils) the relative importance of this catalytic effect might not be readily apparent. The recent findings of Dwight and Riggs [11] support this.

The second hypothesis which can explain the high PTFE volatilization rates observed in this work concerns the possibility of achieving very high polymer/air interfacial areas as the PTFE penetrates into the contacting porous sintered metal substrate. If the volatilization process is diffusion controlled under these prevailing experimental conditions, then the attainment of a high surface to volume ratio would lead to short diffusion path lengths and, hence, to the rapid removal of volatile decomposition products which are assumed to be primarily low molecular weight fluorocarbons [10, 12, 13]. This explanation is favored in view of the extremely thin ($\leqslant$ 100 Å) PTFE films observed in the photomicrographs obtained after the dissolution of the wetproofed gold black.

In view of the commonly accepted view that PTFE thermal degradation is initiated by a random chain scission step followed by a short chain unzipping [10, 14, 15], it is certain that the rapid decomposition of the polymer is accompanied by a correspondingly rapid decrease in average molecular weight to a value much lower than the initial one. This reduction in average molecular weight will likewise lead to a lower melt viscosity, at least in part explaining the low effective viscosities observed in this work [16].

4. Conclusions

The penetration of high molecular weight PTFE into porous sintered gold, sintered nickel and metal blacks (Au or Pt) on heating to temperatures near the melting temperature (335 to 337° C) is most pronounced. Scanning electron microscopic analysis revealed that the metal black particles are enveloped by PTFE films which are on the order of 100 Å thick. Since the penetration distances increase linearly with the square root of time of heating, apparent viscosities can be calculated by means of the Washburn equation. Such derived viscosities are orders of magnitude lower than those expected for the bulk materials. In addition, significant weight losses for the PTFE were observed, indicating volatilization of low molecular weight fragments of the polymer.

The high surface area substrate apparently enables the attainment of very high polymer/air interfacial areas facilitating the rapid removal of volatile decomposition products. Likewise, catalytic effects from the metal surface acting upon the PTFE degradation may become important by virtue of the high metal/PTFE interfacial contact area achievable within the porous metal substrate. The rapid decomposition of the polymer is doubtless accompanied by a decrease in average molecular weight, leading to a lower effective viscosity.

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