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Rheological characterization and thermal degradation of PTFE

Part 2 *The interaction between PTFE and carbon black*

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PTFE ($\bar{M}_n = 5 \times 10^6$), when heated near the melting temperature (335 to 337° C) while in contact with carbon black, is characterized by an effective viscosity and a thermal stability which are orders of magnitude lower than those found in the absence of the contacting high surface area material. The penetration of the PTFE into the porous carbon black occurs by the spreading of a very thin polymer film followed by a thickening of this film with time at temperature until a limiting concentration is reached. The lower the average molecular weight of the PTFE, the more rapidly it penetrates into the porous material. Similar phenomena have been observed with high molecular weight PTFE heated near the melting temperature while contacting high surface area metal blacks or porous sintered metals.

1. Introduction

It has recently been reported that, when high molecular weight PTFE is heated to temperatures near the melting temperature (335 to 337° C) while contacting porous sintered metals and metal blacks, the rheological characteristics and thermal stability of the polymer are very different from those that would be expected based upon the previously reported properties of bulk PTFE [1]. The viscosity of high molecular weight PTFE ($\bar{M}_n = 10^4$ to 10^6) in the range of temperatures between 330 and 350° C has typically been reported to be between 10^{10} and 10^{12} P and, since the rate at which a molten polymer will spread upon a high surface energy material will generally decrease with increasing melt viscosity, good interfacial contact between molten PTFE and porous metal or metal oxide surfaces should be achievable only after very long periods of heating [2–5]. In contrast, viscosities between 10^6 and 10^8 P have been calculated from the measured rates of penetration of high molecular weight PTFE into contacting porous metals (gold and nickel) at 335 to 337° C [1].

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. Although there is mass spectrometric evidence to show that PTFE degradation begins at temperatures as low as 300° C [6, 7], gravimetric methods have generally not been useful as a means to detect PTFE degradation at temperatures below 360° C, and appreciable rates of weight loss are not seen below 425° C ($0.1\% \mathrm{h}^{-1}$) [4]. Nevertheless, rates of volatilization of about $0.1\% \mathrm{h}^{-1}$ have been measured for high molecular weight PTFE heated at 335 to 337° C while contacting porous gold and nickel [1].

In order to determine the thermal characteristics of PTFE when combined with a nonmetallic high surface area material, we have examined the rheological behaviour of the polymer as well as the thermal degradation that occurs when high molecular weight PTFE is heated in the vicinity of the melt temperature while contacting carbon black. As in the case of PTFE heated while contacting 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

The finely divided PTFE material used had, unless otherwise noted, an average molecular weight of approximately 5×10^6. The carbon black was a highly conductive oil furnace black with a surface area of about $250\,m^2\,g^{-1}$ and with an oil absorption value of about $1.80\,cm^3\,g^{-1}$. A layer of the PTFE (with $6\,cm^2$ geometric surface area and containing 2 mg of PTFE per cm^2) was first prepared by filtration of an aqueous dispersion of the polymer upon a porous sintered nickel substrate. A layer of the carbon black (also with $6\,cm^2$ geometric surface area and containing 1 mg of carbon per cm^2) was formed subsequently by filtration of an alcoholic dispersion in such a way that the carbon black and PTFE layers overlapped. The 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 these samples. Water wettability was used as a probe to monitor the penetration of the PTFE into the overlapping carbon black layer as a function of time at temperature. (The experimental sample configuration was the same as that shown in Fig. 1a in [1].) Small droplets of distilled water were placed at various points upon the carbon black layer. Before the sample was heated, the entire carbon black layer was always completely wettable. After a few minutes of heating, however, that portion of the carbon black layer which overlapped the PTFE layer was no longer water wettable. With further heating, a band of non-wettable carbon black was observed to advance from the original PTFE/carbon black interface (see Fig. 1b in [1]). 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 carbon black layer indicated the presence of a fluorine-containing material. (Water wettability measurements were also performed with samples containing overlapping layers of the carbon black and PTFE materials with average molecular weights of about 3.5×10^3, 2.5×10^4, 6×10^4 and 2×10^7.)

Penetration of the PTFE into the overlapping layer of the porous carbon black was also examined as a function of time at temperature by the use of a JEOL JXA-50A electron probe microanalyser. The sample surface was scanned with the electron beam from the region of overlapping PTFE and carbon black far into the portion of the carbon black layer which did not overlap the layer of PTFE. Fluorine concentration profile traces were obtained by recording the intensity of the fluorine sensitive peak as a function of the position of the electron beam. In order to determine the relationship between the fluorine peak intensity and the PTFE concentration, PTFE-carbon black mixtures of varying composition were prepared, and layers of these mixtures were formed by filtration upon sheets of the porous sintered nickel substrate. These samples were heated in the air for 15 min at 335 to 337° C, and their surfaces were subsequently scanned with the electron probe to obtain the required plot of microprobe peak intensity versus PTFE concentration.

The scanning electron microscope was also used to investigate the penetration of PTFE into the contacting carbon black. A $2\,mg\,cm^{-2}$ layer of PTFE was formed by filtration upon a sheet of the porous nickel substrate as described above. A $1\,mg\,cm^{-2}$ layer of the carbon black was subsequently filtered directly onto the PTFE layer, and the sample was heated in the air for 15 min at 335 to 337° C. The carbon was then gradually removed from the sample by leaching with a hot oxidizing acid solution made by mixing $100\,cm^3$ concentrated H_2SO_4, $100\,cm^3$ concentrated HNO_3, and $5\,g\,K_2Cr_2O_7$ (boiled down to about $140\,cm^3$ total volume). The temperature employed in the leaching operation was 120° C. Sections of the sample were removed for later microscopic examination after successive 30 s periods of leaching. To facilitate the scanning electron microscopic analysis, the cleaned and dried sample sections were sputter coated with a 100 Å layer of platinum.

The thermal degradation of the polymer was monitored gravimetrically using samples supported upon metallic gold substrates (to avoid any ambiguity arising from possible changes in the weight of a nickel substrate). These samples all contained about 5 g carbon black and the amount of PTFE necessary to make the overall composition somewhere between 10 and 70% PTFE.

Some of the samples, prepared as were the samples meant for electron microscopic examination described above, consisted of a layer of PTFE filtered directly onto a layer of carbon black supported upon a sheet of porous sintered gold. The remaining samples were prepared by the filtration of a mixture of the two components upon a sheet of the porous gold substrate. These samples were all heated in the air at 335 to 337° C and were weighed periodically using a Mettler analytical balance. For the purposes of comparison, weight loss measurements were performed simultaneously upon two other samples. One of these control samples was prepared by depositing 8.6 mg of the PTFE upon a piece of smooth gold foil. The other consisted of 5.3 mg of carbon black filtered onto one of the porous gold substrates.

3. Results and discussion

The results of the electron microprobe examination of a sample consisting of overlapping layers of PTFE and carbon black (after heating for 100 min at 335 to 337° C) are shown schematically in Fig. 1. (This fluorine concentration profile trace is representative of those obtained with other heating times.) The trace can be divided into four characteristic regions for purposes of analysis. The first region (from −9 to −2 μm in the figure) corresponds to the area of overlap of the PTFE and carbon black filtered layers. The fluorine peak intensity is highest here. In the second region (from −2 to +2 μm in the figure), the fluorine peak intensity decreases sharply. This region corresponds to the original PTFE-carbon interfacial boundary region (the perimeter of the filtered PTFE layer). The third region (from +2 to +25 μm in the figure) is characterized by a relatively constant fluorine peak intensity, the magnitude of which is only about a tenth of that measured in the region of overlap of the PTFE and carbon black layers. In the fourth region (from +25 to +49 μm in the figure), the fluorine peak intensity decreases in an approximately linear fashion from the value characteristic of region three to the background value found for carbon black heated in the air at 335 to 337° C in the absence of a contacting layer of PTFE. It is found that, as the time of heating is increased, the widths of the third and fourth regions both simultaneously increase. The magnitude of the fluorine peak intensity corresponding to region three does not, however, change significantly as the time of heating is varied.

By the use of the PTFE-carbon black mixtures of known composition, it was found that the fluorine peak intensity measured in region three of the concentration profile trace corresponds to a PTFE-carbon composite containing about 35%

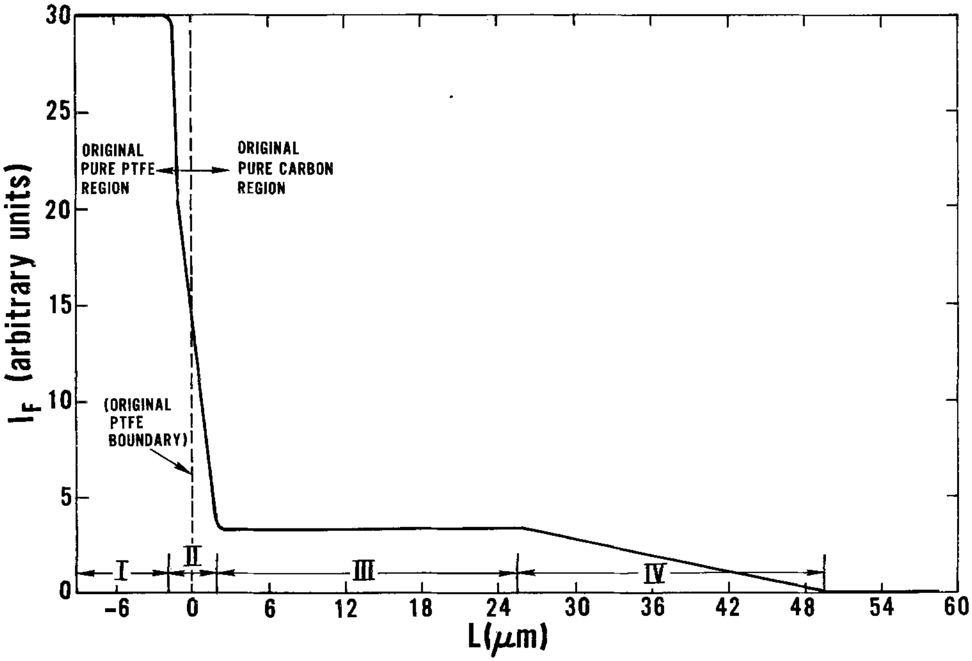

Figure 1 Electron microprobe fluorine concentration profile trace: PTFE penetration into an overlapping layer of carbon black after 100 min at 335 to 337° C.

PTFE. This is apparently the maximum composition attained when an excess of the PTFE is allowed to penetrate into the carbon black under the conditions of our experiments. Region four of the concentration profile trace thus corresponds to a portion of the carbon layer into which the PTFE has penetrated to less than the maximum extent. The fluorocarbon distribution in region four was analysed as a function of the time of heating (referring to the PTFE-carbon black mixtures of known composition) to yield the results shown in Fig. 2. The distance from the original boundary of the filtered PTFE layer has been plotted versus the square root of the time of heating for concentrations of 15 and 30% PTFE. Linear penetration distance versus $t^{1/2}$ plots are obtained, as was previously found for PTFE penetration into contacting porous gold and oxide-covered nickel at 335 to 337° C [1].

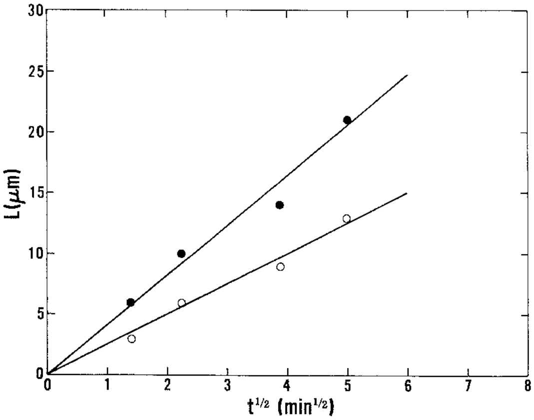

Figure 2 PTFE penetration into an overlapping layer of carbon black at 335 to 337° C: electron microprobe data. (●) 15% PTFE; (○) 30% PTFE.

Owing to the observed linear relationships, the Washburn equation for capillary flow, Equation 1, can be applied to obtain at least an order of magnitude estimate of the apparent viscosity of the high molecular weight PTFE sample.

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

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 (0.01 to 1.0 μm), and θ the contact angle (assumed to be 0°). Using these values, the data corresponding to a PTFE concentration of 30% (almost the maximum attainable concentration) yield a cclculated viscosity of between 10^4 and 10^6 P, values several orders of magnitude smaller than the commonly accepted viscosity range and even smaller than those calculated previously from the rates of penetration of the same PTFE material into contacting porous gold and oxide-covered nickel.

In view of the anomalously low effective viscosity of the high molecular weight PTFE heated near the melting temperature while contacting the carbon black, the thermal stability of the PTFE was examined under the same experimental conditions. The PTFE-carbon black samples used contained between 10 and 70% PTFE and consisted either of contacting layers of the PTFE and carbon black or of a mixture of the two materials. (All samples were supported upon porous sintered gold substrates.) For purposes of comparison, the thermal stabilities of the high molecular weight PTFE (supported upon a smooth gold foil substrate) and of the carbon black (filtered onto one of the porous gold substrates) were also determined.

The experimental results are plotted in Fig. 3 as percentage volatilization versus time at 335 to 337° C. (Only the points for the PTFE-carbon black samples containing approximately equal amounts of the two materials have been plotted since they are representative of the data obtained with other sample compositions.) The weight loss of the PTFE supported upon a smooth gold foil substrate was negligibly small during the more than 200 h at temperature. In contrast, the pure carbon black sample lost about 20% of its initial weight (presumably as CO_2) during 230 h of heating. The two PTFE-carbon black composite samples both volatilized at about the same rate as the sample containing only carbon black. In general, no distinction was found between the data corresponding to the samples containing contacting PTFE and carbon black layers and that corresponding to samples made by filtering the components onto the porous gold substrates. Neither was there any discernable correlation based upon composition. Thus, under the conditions of our experiments, the rate of carbon weight loss due to oxidation is about the same as the rate of PTFE volatilization resulting from thermal degradation (a result which must be assumed to be purely coincidental).

It is not surprising that the high molecular

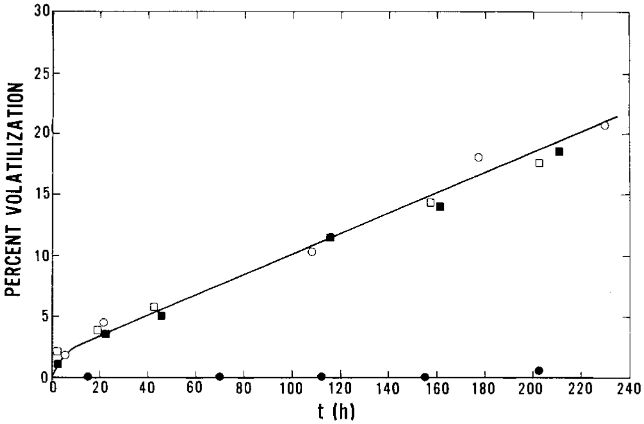

Figure 3 Volatilization of PTFE carbon black and PTFE-carbon black composites at 335 to 337° C ($6\,cm^2$ layers). (●) 8.6 mg PTFE (on gold foil); (○) 5.3 mg carbon black; (■) 4.5 mg PTFE on 4.5 mg carbon black; (□) 6.4 mg PTFE mixed with 5.5 mg carbon black.

weight PTFE material exhibits a negligible rate of thermal degradation when heated in the air at 335 to 337° C while in contact with a smooth high surface energy material like metallic gold foil. As previously described, this is the expected result in view of many previous investigations of PTFE thermal degradation. The surprising result is that this is not the case when the high molecular weight PTFE is similarly heated while contacting porous high surface energy materials like carbon black. The high rates of volatilization measured under these conditions must certainly be the direct result of the penetration of the PTFE into the porous materials. Thus, the fact that no difference was found between the rates of PTFE volatilization measured with samples originally composed of contacting layers of PTFE and carbon black and with samples originally containing mixtures of the two materials is to be expected based upon the rapid penetration of the PTFE into the carbon black under the experimental conditions employed. That no correlation was found between volatilization rates and composition (over the range of composition examined here) is understandable since, even if the PTFE were only to penetrate into pores with diameters greater than about 0.1 μm, the resulting polymer films would still be no more than a few hundred Angstroms thick for any of the compositions employed (assuming the PTFE to be uniformly distributed throughout the porous carbon black).

Indeed, the scanning electron microscope revealed that a honeycomb network of thin PTFE films remains after the dissolution of the carbon from a sample originally consisting of contacting layers of PTFE and carbon black heated for 15 min at 335 to 337° C. In Fig. 4 are shown typical high resolution electron micrographs of the surface of this porous PTFE sturcture. The walls of this filmy PTFE structure are very thin, being apparently not much thicker than the 100 Å platinum coating which had been sputtered onto the sample surface to facilitate microscopic examination. The effective cell diameter is approximately 0.2 μm (about the size of a carbon black particle aggregate).

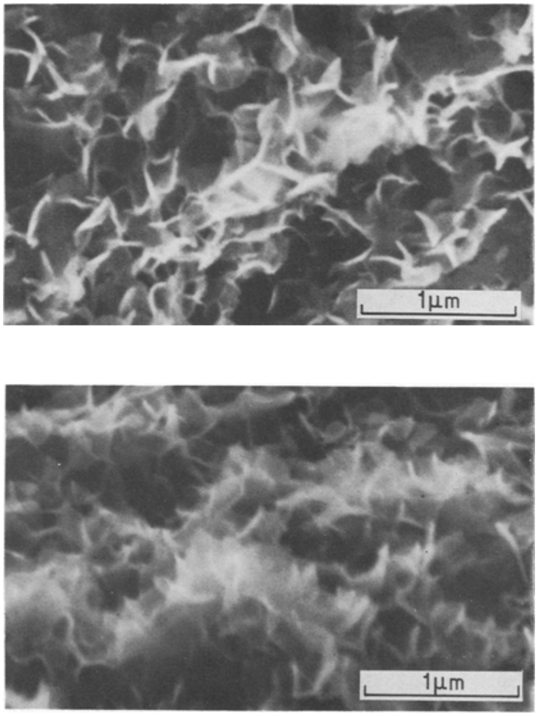

Figure 4 High resolution electron micrographs of the porous PTFE structure remaining after removal of the carbon from a 50% PTFE–50% carbon black mixture heated for 15 min at 335 to 337° C.

As has been demonstrated for the case of PTFE penetration into contacting layers of gold and platinum black [1], room temperature water wettability can also be used as a probe to determine the distance of penetration of the high molecular weight PTFE into a contacting carbon black layer as a function of time at temperature. The quantitative results, obtained with samples containing PTFE materials with average molecular weights ranging between 3.5×10^3 and 2×10^7, are presented in Fig. 5 where the width of the wetproofed band of carbon black is plotted versus the square root of the time at 335 to 337° C. As before, the width of the wetproofed carbon band (assumed to be at least proportional to the greatest distance of penetration of the wetproofing material) generally increases approximately linearly with the square root of the time of heating. However, in the case of the PTFE material with the lowest average molecular weight ($\bar{M}_n \approx 3.5 \times 10^3$), the entire carbon black layer was found to be non-wettable after the briefest period of heating (shown by the dashed line in Fig. 5). On the other hand, in the case of the PTFE material with the highest average molecular weight ($\bar{M}_n \approx 2 \times 10^7$), no wetproofing was seen even after 64 h heating. Taken as a whole, these data indicate that the lower the average molecular weight of the PTFE, the more rapidly it penetrates into the porous carbon.

If Equation 1 is applied to the data corresponding to the PTFE material with $\bar{M}_n \approx 5 \times 10^6$, a value of between 4×10^2 and 4×10^4 P is obtained for the effective viscosity of the high molecular weight PTFE. The apparent contradiction between the flow rates (and, therefore, also the effective viscosities) calculated from the water wettability data (Fig. 5) and the electron microprobe data (Fig. 2) for this PTFE-carbon black system (as well as for other PTFE-porous material systems) is explicable by referring to the representative fluorine concentration profile trace shown in Fig. 1. As previously indicated, the penetration of PTFE into a contacting porous material is not characterized by a simple well-defined front of flowing polymer. Quite the contrary. For any given time of heating, the PTFE concentration at the limit of penetration is actually very low, so low as to be perhaps undetectable by any means except that used here – the reduction of the substrate wettability as a result of the presence of the fluoropolymer. Thus, far from the original source of the penetrating PTFE, the polymer must be present in the form of an extremely thin film. Proceeding from the limit of penetration to the source of the penetrating PTFE, the polymer concentration increases (region 4 in Fig. 1) until the apparent saturation concentration is reached (region 3 in Fig. 1).

The picture that, therefore, emerges of the way in which PTFE penetrates into carbon black (and other porous materials) involves first the spreading of a very thin polymer film followed by a thickening of this film with increasing time at temperature until the limiting concentration is reached. The possible causes of the very high rates of decomposition observed for PTFE heated in the vicinity of the melting temperature while contacting porous high surface area materials have been discussed elsewhere [1]. Suffice it to say that, in view of the commonly accepted idea that PTFE thermal degradation is initiated by a random chain scission step followed by a short chain unzipping [8–10], it is certain that the rapid decomposition of the polymer indicated by the gravimetric measurements is accompanied by a correspondingly rapid

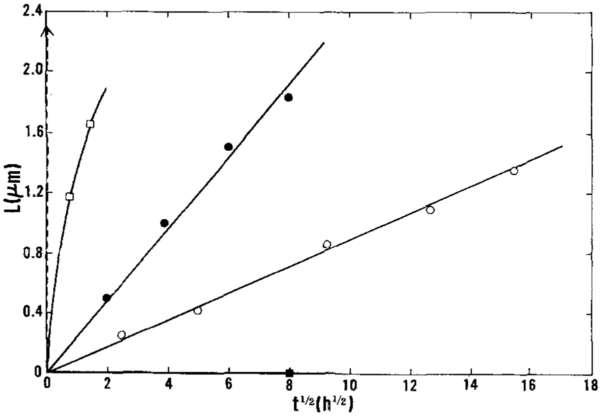

Figure 5 PTFE penetration into an overlapping layer of carbon black at 335 to 337° C: water wettability data. (– – –) $\bar{M}_n \approx 3.5 \times 10^3$; (□) $\bar{M}_n \approx 2.5 \times 10^4$; (●) $\bar{M}_n \approx 6 \times 10^4$; (○) $\bar{M}_n \approx 5 \times 10^6$; (■) $\bar{M}_n = 2 \times 10^7$.

decrease in average molecular weight to a value much lower than the initial one. The reduction in average molecular weight will likewise lead to a lower effective viscosity and, hence, a more rapid rate of PTFE penetration into the porous material [11].

4. Conclusions

The penetration of high molecular weight PTFE into contacting carbon black (and other porous materials) on heating to temperatures near the melting temperature (335 to 337° C) is unexpectedly rapid and occurs by the spreading of a very thin polymer film followed by a thickening of this film with increasing time at temperature until the limiting concentration is reached. The lower the average molecular weight of the PTFE, the more rapidly it penetrates into the porous material. Scanning electron microscopic analysis reveals that the carbon black particles are enveloped by PTFE films which are on the order of 100 Å thick. Since the penetration distance increases linearly with the square root of the 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 polymer. It has also been found that, presumably as a result of the penetration of the PTFE into the porous carbon black, the polymer volatilizes many times faster than it does in the absence of a contacting porous substance.

The factors contributing to the widely differing rheological and thermal characteristics of PTFE in the presence or absence of a contacting high surface area material have not as yet been fully determined. The effects of surface chemical and morphological characteristics upon these properties as well as upon the adhesion of PTFE to contacting metallic and non-metallic surfaces need to be explored.

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