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POLYMERIZATION-FILLING OF POLYTETRAFLUOROETHYLENE

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Abstract—Polymerization of tetrafluoroethylene (TFE) in an aqueous medium using a redox system in the presence of a hard disperse filler leads to polymerization-filled polytetrafluoroethylene (PTFE). The influences of various factors on the polymer yield, the conversion of TFE and the degree of filling were studied. The kinetic dependencies concerning the polymerization-filling of PTFE with $CaCO_3$ were studied. The reaction order, activation energy and the ratio of rate constants for chain propagation and termination were determined.

INTRODUCTION

The traditional methods for obtaining compositions based on polytetrafluoroethylene (PTFE) are dry mechanical [1] and wet [2] mixing of the components, i.e. polymer and filler. For these methods, special equipment and considerable material and energy resources are necessary. From this point of view, it is probably better to use the method of filling by polymerization [3–6] which consists of polymerization of the monomer on the surface of the filler, i.e. during the polymer synthesis. Various materials (natural and modified) can be used as fillers including kaolin, talc, silica, asbestos, metal salts and oxides, graphite, glass-fibres, ceramics [6].

The advantages of polymerization filling lie mainly in avoidance of several steps in the composition preparation (grinding, fractioning, homogenization, granulation, etc.). During the polymerization, the filler surface is covered with a dense polymer film, i.e. part of the filler is encapsulated within the polymer phase so preserving the processing equipment from abrasion. Further, during polymerization-filling, covalent bonds may form between filler and polymer particles [7]; it is also possible to obtain compositions with higher degrees of homogeneity and filling, which may be processed either alone or as master-batches [8].

There seem to be no publications on polymerization filling of PTFE in aqueous systems. It is of considerable interest both for obtaining monolithic compositions and gas-filled polymers. In the present work, the influences of the polymerization conditions, the nature and filler content on the polymerization-filling of PTFE were studied. Some aspects of the kinetics of polymerization-filled PTFE were also investigated.

EXPERIMENTAL PROCEDURES

Tetrafluoroethylene (TFE) was 99.5 to 99.8% pure, obtained through debromination of 1,2-dibromotetrafluoroethane (Freon 114 R-B_2).

The polymerization-filling was carried out in an aqueous system using a redox system consisting of $(NH_4)_2S_2O_8$ (initiator) and $AgNO_3$ (activator) in the ratio 1 : 1 and $Na_2B_4O_7 \cdot 10H_2O$ (buffer agent) in the presence of filler. The polymerization procedure was described previously [9]. The polymerization takes place at 291 K, in a semiflow system at constant pressure 1.8 ± 0.05 MPa and 800 min^{-1} stirring speed.

Kinetic study of the polymerization was conducted batchwise. TFE concentration in the aqueous system was measured by using the Henry equation and a procedure already described [10].

After the end of the reaction, the unreacted monomer was removed and the obtained PTFE (Buflon-3 Norplast) was washed with warm water, filtered and dried in vacuum to constant weight.

RESULTS AND DISCUSSION

To examine the influence of various factors on the degree of filling and the conversion of TFE, polymerization-filling of PTFE was carried out in the presence of several fillers viz. $CaCO_3$, Al_2O_3, TiO_2 and SiO_2. The nature of the filler was found to have considerable effect on the polymerization rate (Table 1). For the fillers under investigation, the best results were obtained with $CaCO_3$. A systematic study of polymerization-filling of PTFE was therefore carried out with that material.

The enthalpies of crystallization (ΔH_c) and melting (ΔH_m) of the synthesized products increase with decrease of the degree of filling (Table 1). This effect is probably connected with the influence of the hard-disperse filler on the nuclei arising in the crystal phase. The melting temperature (T_m) of the composites, according to DSC data, is the same at 606 K, and the crystallization temperature (T_c) increases significantly with the degree of filling. The decomposition temperature, according to DTA data, decreases with increase of the degree of filling (Table 1).

Figure 1 shows that the conversion of TFE (curve 2), and the PTFE–Norplast yield (curve 1) increases nearly linearly with polymerization time. The degree of filling decreases because the quantity of filler in the polymerization medium is fixed while the quantity of the newly synthesized polymer increases (curve 3). There are several possibilities to vary the

Table 1. PTFE

Filler	General polymerization rate (g/hr)	Conversion (%)	Degree of filling (%)	Physical properties				
				T_c (K)	T_m (K)	ΔH_c (J/g)	ΔH_c (J/g)	T_d (K)
Al_2O_3	3.7	13	66	590	602	17.0	16.8	633
TiO_2	6.1	22	42	585	606	38.6	35.6	—
SiO_2	3.0	22	33	585	602	47.0	44.4	733
$CaCO_3$	11.1	42	25	586	606	48.7	42.5	743
$CaCO_3$	10.3	35	30	585	606	45.3	43.4	723
$CaCO_3$	9.6	24	42	586	606	39.4	36.8	721
$CaCO_3$	9.0	15	55	589	606	27.7	28.5	693

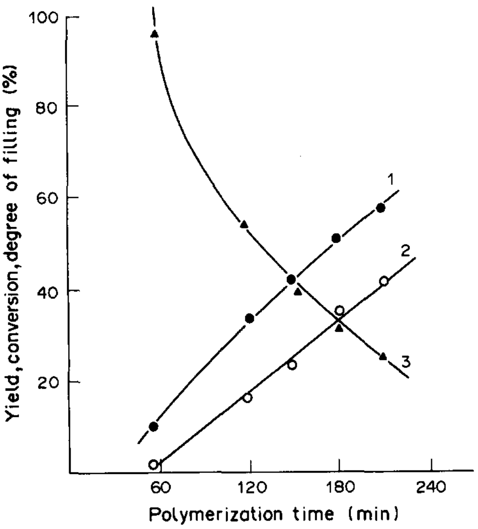

Fig. 1. Dependence of yield (curve 1), conversion (curve 2) and degree of filling (curve 3) on polymerization time.

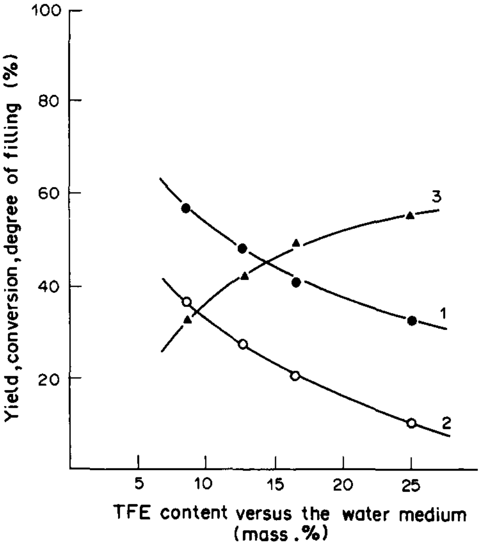

Fig. 3. Dependence of yield (curve 1), conversion (curve 2) and degree of filling (curve 3) on the TFE content relative to the water phase.

compositions. Under the chosen conditions by changing the polymerization time, the degree of filling can be varied over a wide range (from 5 to 90%) at an average polymerization rate of 16 g/hr.

The influence of the concentration of the initiating system on the composition of the product was also studied. Figure 2 shows that change in the initiator concentration (from 0.005 to 0.020 mass. %) has a considerable effect on the degree of filling (from 25 to 98%). At high monomer conversion, as a result of the increase in the polymer content, stirring of the system becomes difficult.

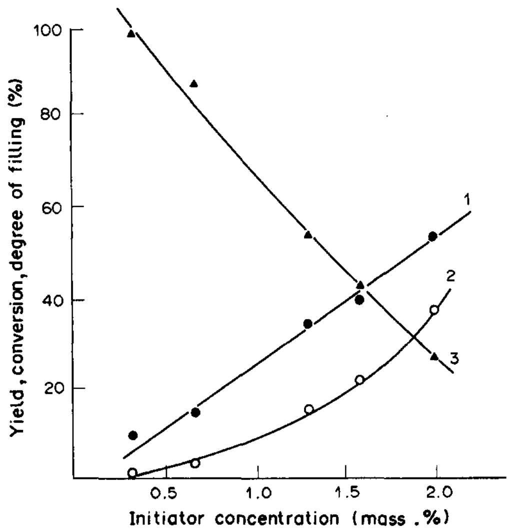

Fig. 2. Dependence of yield (curve 1), conversion (curve 2) and degree of filling (curve 3) on initiator concentration.

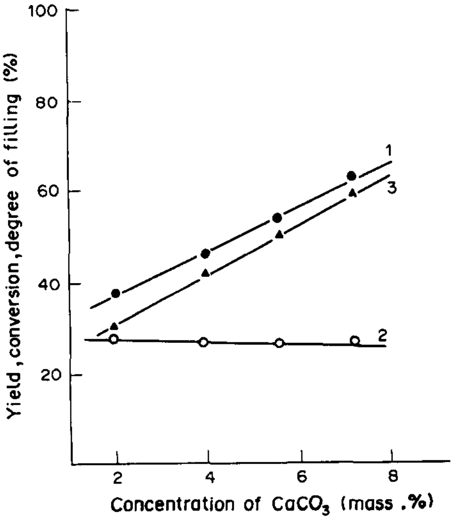

Fig. 4. Dependence of yield (curve 1), conversion (curve 2) and degree of filling (curve 3) on the filler concentration ($CaCO_3$).

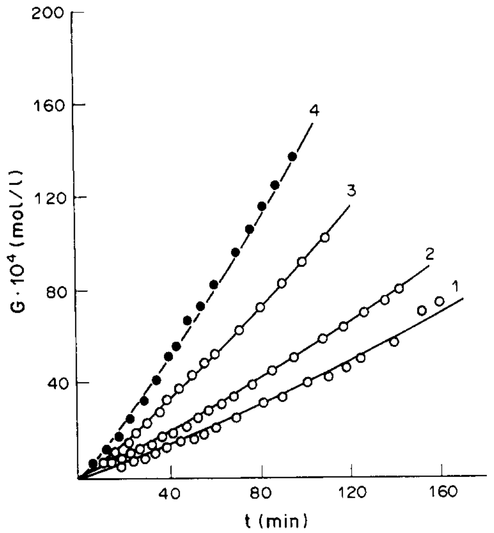

Fig. 5. Kinetic curves of polymerization-filling on PTFE with $CaCO_3$ at various initiator concentrations: 1, 8.8×10^{-5}; 2, 1.1×10^{-4}; 3, 1.3×10^{-4}; 4, 1.8×10^{-4} mol/l. G, consumed TFE.

The influence of the ratio TFE : water on the degree of filling is shown in Fig. 3. The highest yield was obtained at a TFE content in the reaction medium of 9.09 mass. % relative to water. It is probably governed by diffusion rather than kinetic factors.

It is well known, for the polymerization-filling of other polymers, that the nature and the concentration of the filler have considerable effects on the rate of the process and the polymer structure [3].

The influence of $CaCO_3$ concentration on the polymerization-filling of PTFE is shown in Fig. 4. The concentration of the disperse filler does not greatly affect the TFE conversion, or the polymerization rate (curve 2), probably because of the non-activated surface of the $CaCO_3$. It should be noted that, with increase of the filler concentration, there is increase in the quantity of $CaCO_3$ not involved in the polymer composition.

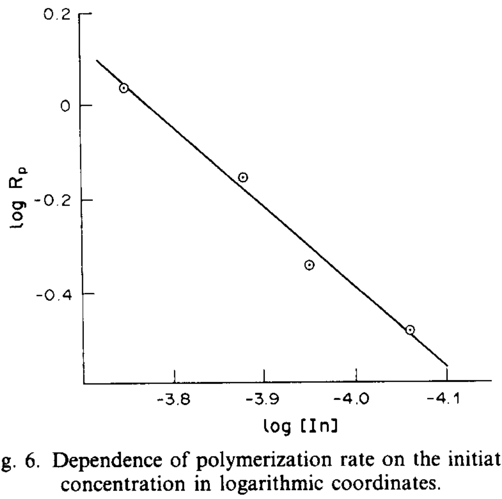

Fig. 6. Dependence of polymerization rate on the initiator concentration in logarithmic coordinates.

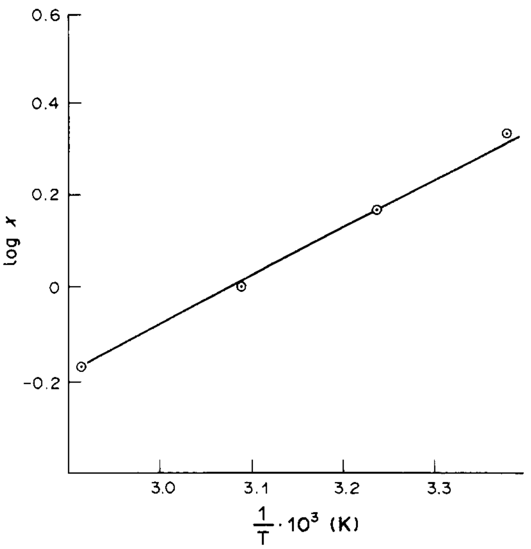

Fig. 7. Temperature dependence of the transformation coefficient x of polymerization-filling of PTFE with $CaCO_3$.

Kinetic curves of polymerization-filling of PTFE with $CaCO_3$ are shown on Fig. 5. The polymerization in the presence of a filler proceeds under stationary conditions and, contrary to homopolymerization, no autoacceleration takes place.

The rate of polymerization (R_p) was determined from the slope of the initial part of the kinetic curve (Fig. 6). R_p was found to be proportional to the initiator concentration to a power of 1.75. The high value of this exponent is likely to be associated with chain-transfer reactions. Chain-transfer probably occurs on the filler surface, because other processes of a similar type are unlikely. A parallel graft-copolymerization of short PTFE chains onto the filler surface is quite possible for polymerization in the presence of $CaCO_3$.

The ratio between rate constants of chain propagation and chain termination was also determined and found to be $k_p/k_t^{0.5} = 8.1 \times 10^{-2}$, whereas $k_p/k_t^{0.5} = 7.4 \times 10^{-2} l^{0.5}/mol^{0.5} \cdot sec^{0.5}$ for homopolymerization. The difference corresponds to an increase of k_t on the solid phase if k_p is constant under the conditions studied.

The apparent activation energy of polymerization-filling from the Arrhenius plot (Fig. 7) was −19.5 kJ/mol. The rate of the process decreases with rising reaction temperature. This effect may be governed by the desorbtion of the monomer from the water phase. Presumably, the localization of radical generation in the surface zone around the filler results in orientation of the monomer molecules to the solid phase surface. However, at higher temperature, they desorb onto the surface of the water phase and the rate of the process decreases.

The polymerization-filled PTFE obtained under various condition is a mixture of PTFE particles, agglomerates of filler and polymer particles, filler particles encapsulated in polymer, grafter PTFE chains onto the filler surface and some filler particles uninvolved in the polymer phase (Fig. 8).

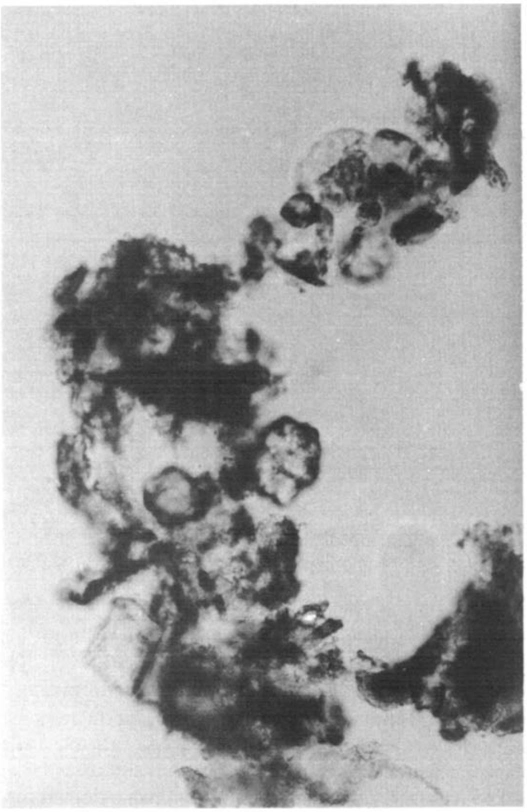

Fig. 8. Photomicrograph of polymerization-filled PTFE. Parallel polarizers, × 125.

CONCLUSION

Through polymerization in aqueous medium using a redox system in the presence of hard disperse fillers ($CaCO_3$, Al_2O_3, TiO_2 and SiO_2), polymerization-filled PTFE was obtained.

The influences of various factors on the polymer yield, the conversion of TFE and the degree of filling were studied for the case of $CaCO_3$. It was found that, by varying the component concentrations and the polymerization conditions, Buflon-3 Norplast containing 5–60% $CaCO_3$ can be obtained, with crystallization temperature from 585 to 589 K, melting temperature 606 K and decomposition temperature from 693 to 743 K.

Based on Buflon-3 Norplast synthesized with a $CACO_3$ concentration of 40–60 mass. %, microporous membrane filters are formed. The properties of the membrane filters so obtained are being examined.

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