Shock Wave Treatment of Polytetrafluoroethylene: Structure and Properties

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Abstract. The paper considers changes of the structure and thermomechanical properties of polytetrafluoroethylene pressing after the explosive treatment depending on the thickness of the pressing. Structural changes and defects in samples, preserved even after sintering, were detected.

1. Introduction

Purposive modification of fluoropolymers to change their structural organization and controlled variation of properties is one of the most urgent tasks in modern polymer materials science which has great practical importance in the development of materials with increased thermal and heat resistance. Currently different processing methods based on the use of external energetic influences: pyrolysis, radiation, laser and ultrasonic processing et al. are developed [1, 2, 3]. Explosive treatment (ET) is promising for polymers and composites on their basis which by the actuation of high speed shock wave in the solid provides the realization of both high pressure (up to 10 GPa) and temperatures (up to 1000 °C). This causes different activating physical (compaction, crushing, deformation and welding of the particles) and chemical (destructively-recombinalional and mechanochemical reactions) transformations of the polymer [4-7]. It is determined that the modification of polymer materials, especially by high-energy impacts (including explosive treatment) leads to considerable changes in their structure, physico-chemical and mechanical properties, thereby converting the polymer to an activated state. ET is a multifactorial process, and the intensity of transformations is adjusted by changing of process parameters of the loading and the properties of the treated polymer powder. This paper presents the results of research of the ET influence on the structural changes effecting on the thermomechanical properties of polytetrafluoroethylene (PTFE).

2. Study subject

The work researched the influence of various ET parameters on the structure formation and thermomechanical properties during the production of PTFE compacts (GOST 10007-80) of various thickness (0.8 and 3.2 mm). ET was realized by the flat loading with the sliding shock front (SF) with a detonation velocity of explosive 1680 ms⁻¹. Pulse of pressure (P) in the pressing powder depends not only on the power of the explosion, but also on the thickness of the pressed material. Increasing the height of the pressed powder with the same explosives reduces the pressure of ET and simultaneously extending its effect (τ). Thus, while ET of pressings 0.8 mm calculated values were P = 0.7 GPa and τ =13 ms (sample #1), and for 3.2 mm - P = 0.3 GPa and τ = 43 ms (sample #2).
3. Methods
The density ($\rho$) was determined by hydrostatic weighing using the analytical weighing system Shinko HTR-220SE GOST 15139-69. Structural changes were considered by a scanning electron microscope of FEI Versa 3D DualBeam and diffractometer "DRON-3.0" in the radiation of a copper anode CuK$_\alpha$, analyzing the profiles of reflections with 100 and 003 indexes. Correlation of structures and thermal properties was determined by the thermomechanical analysis (TMA) 402 F3 Netzsch Hyperion by standard methods, by detecting deformations caused by penetration of the indenter into the sample under load 1N and heating velocity of 5 °C/min.

4. Results and discussion
The research shown, that the maximum compaction is reached after ET (pressings density is $2.2 - 2.28$ Mg/m$^3$). Subsequent sintering doesn’t change the density of the most thin samples ($\rho = 2.23$ Mg/m$^3$), and with the increase of thickness of pressing density reduces by 10% in the sample with thickness of 3.2 mm, due to the specialties of the PTFE crystalline phase melting during sintering and shrink ripple.

While studying the morphology (figure 1) of cleavage surface of the sample #2 (P = 0.3 GPa, $\tau$ = 43 ms), dense areas were found out (figure 1 a), and at a higher magnification (figure 1 c) - packless short fibrillar areas. In such a case, a level of interparticle interactions and properties reduce.

Samples with smaller thickness #1 (P = 0.7 GPa, $\tau$ = 13 ms) have consolidated particles and packless areas are not detected (figure 1 b). PTFE particles are considerably flattened in the direction of shock compression in both cases (figure 1 c, d), and dense formations are similar to the layered structures in fluoroplastic.

![Figure 1. SEM images of PTFE after sintering and ET:](image)
a, b - $\delta = 3.2$ mm, c, d - $\delta = 0.8$ mm
At high magnifications (figure 1 d) sample #1 shows dense oriented lamellar structure that is not found in other samples, which confirms more intense deformation of particles of thin layers in the ET. The energy dispersive analysis indicates the absence of destructive processes in the ET: the elemental composition of the PTFE is almost the same for all samples, and identical to that of the original polymer.

Research of the supramolecular structure of the samples by X-ray analysis showed, that amorphous crystal structure of PTFE remains with a high degree of crystallinity (65-71%), the crystalline peak at $2\Theta = 18^\circ$ and diffuse halo in the region of $2\Theta = 40-50^\circ$. However, the sample №2 revealed more intense changes in crystal structure in comparison with the thin sample №1. The broadening of the main reflex of crystalline phase (100) is mostly caused by crushing of crystalite size, which decreases more than 2 times from 38 to 15 nm, and the relative strain of the crystal lattice increases by 20% (table 1). Such changes are caused by the fact, that the mechanical resistance of the the polymer has ductile nature, and the effective in the explosive loading is not only the value of the impact pressure, but also pretty much its influence duration, the value of which in the sample №2 is 3 times (43 ms) bigger. The degree of crystallinity of PTFE with increasing of density of pressing under the conventional methods of processing should increase, but for the more dense sample №1 it is below 5% as well as after the radiation exposure of the polymer [8], when an increase of the radiation dose leads to the increase of the density of the material and simultaneously reduces crystallinity $\chi$.

| Thickness , $\delta$ (mm) | $\chi$ (%) | Structural defects | $D$ (nm) | $\beta$ (mrad) | $\Delta d/d$ $(10^{-3}$ rad) |
|--------------------------|------------|--------------------|---------|----------------|------------------|
| 0.8                      | 65         |                    | 38      | 2.92           | 4.43             |
| 3.2                      | 71         |                    | 15      | 3.36           | 5.27             |

Changes occurring in the morphology and supramolecular structure of PTFE with the ET influence its thermomechanical properties (figure 2, table 2). The results of thermomechanical analysis (TMA) correlate with the results mentioned above. The residual porosity in the sample №2 leads to penetration of the indentor while heating, and its absence leads to expand of hard-grained sample №1. Amplification of intermolecular and interparticle interactions, as well as minimal crystal structure imperfection in sample №1 led to the PTFE melting point elevation from 327 to 340 °C. Alternatively, the melting point of sample №2 almost corresponds to the melting point of the primary polymer (327 °C).

| $\delta$ (mm) | Softening | Relative deformation $\varepsilon$ (%) at temperatures (°C) |
|---------------|-----------|----------------------------------------------------------|
|               | $t$ (°C) | $\varepsilon$ (%) | 200 | 250 | 300 | 350 | 390 |
| 3.2           | 325      | 6             | 2   | 3.5 | 5   | 12  | 14  |
| 0.8           | 340      | 3             | -2  | -0.5| 0.5  | 22.5| 24  |
5. Conclusion

Therefore, it is determined that changes in the ET parameters (P from 0.3 to 0.7 GPa) and the pulse duration (from 13 to 43 ms) are accompanied by changes of the structural organizations and allow to adjust the degree of compaction, structure, interparticle interaction in PTFE. Quantitative criteria of parameters of PTFE explosive treatment (P=0.7 GPa, $\tau = 13$ ms) are determined, with the achievement of maximum bodying and minimal crystal structure imperfection, which allowed to produce the material with high heat resistance and melting point of 340 °C.

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