

Ultrasonication-Induced Changes in Physicomechanical and Tribotechnical Properties of PTFE Composites

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Abstract. The effect of ultrasonication on PTFE and its composites with zeolite and fluoroplast F-4NTD-2 was studied. Ultrasonication was found to cause changes in the supramolecular structure, and consequently, the tensile strength, relative elongation, and mass wear rate. Changes in the topology of the materials following ultrasonication were investigated by scanning electron microscopy. The optimum enhancement of the desired properties was found in the PTFE composite containing 2% activated zeolite.

Key words: Polytetrafluoroethylene, Polymer composite, Ultrasonication, Supramolecular structure, Tribotechnical property, Physicomechanical property

INTRODUCTION

Various methods have been proposed to improve the physicomechanical and tribotechnical properties of polymers. The addition of nanomaterials,¹⁻³ and the effects of mechanical activation,⁴⁻⁶ ion plasma treatment,^{7,8} ultrasonication^{9,10} and microwave irradiation^{11,12} on polymers have been extensively investigated in order to improve their physicomechanical and tribotechnical properties. Of these, ultrasonication is widely employed, in which ultrasonic frequencies (>20 kHz) are used to agitate the particles in a system, leading to both chemical and physical transformations. Extensive research has been dedicated to elucidating the effects of agitation and irradiation over different wavelengths on the cross-linking and supramolecular properties of polymers.^{13,14} Consequently, ultrasonication has been shown to be one of the most effective means to change the surface energy of polymer materials and to modify their properties.⁹

Although ultrasonication, i.e., the cyclic deformation of a polymer material at ultrasonic frequencies, has been extensively investigated in solution,^{9,10} very few studies have been conducted on the solid phase materials.¹⁵⁻¹⁷ In 1995, Gendron *et al.* reported that ultrasonication during the processing of polymers such as polystyrene, polypropylene, and polyethylene caused increased adhesive interaction among the polymer chains.¹⁵ However, they did not investigate the effect of pre-processing ultrasonication on the polymer materials.

In this work, we report on the effect of pre-processing ultrasonication on a solid polymer and its composites.

EXPERIMENTAL

Polytetrafluoroethylene (PTFE)¹⁸ was used as the polymer matrix because it possesses good anti-friction characteristics and is chemically inert and frost resistant. However, some of the disadvantageous properties of PTFE that need improvement are its low tensile strength, relative elongation, and low wear resistance under load, which can limit its practical application under severely stressful conditions, such as very low temperatures. The additives used were fluoroplast F-4NTD-2 (a low-molecular-weight PTFE with particle sizes ranging from 5 to 30 μm, used as a dry lubricant in friction joints and as an additive to aid oil viscosity¹⁹) and activated natural zeolite.²⁰ The natural zeolite used in this study was sourced from the Hongurou Deposit, the Republic of Sakha (Yakutia), Russian Federation. Ultrasonication was performed using a 35 kHz Laborette 17 ultrasonic bath with a working volume of 4 L.²¹ Ultrasonication of PTFE powder and its composites was conducted at room temperature for 10–60 min. PTFE and F-4NTD-2 powders were mixed under dry conditions and subsequently combined with activated natural zeolite. The activated natural zeolite was prepared by pulverizing natural zeolite for 2 min in a planetary mill.²² The particle size of the activated zeolite

was in the range of 30–900 nm, and the specific surface area was increased to $1.7 \times 10^4 \text{ m}^2/\text{g}$.²³ The resulting mechanically activated zeolite was treated with $5 \times 10^{-3} \text{ mol/L}$ sodium stearate in aqueous media, and then isolated and dried. Finally polymer composites were made by ordinary polymer processing, and the physicochemical and tribotechnical properties were investigated.

The tensile strengths and relative elongations of the polymer composites were investigated according to the Russian State standard method (GOST-11262-80).²⁴ Friction coefficients of the polymer composites were determined by the Russian State standard method (GOST 11629-75)²⁵ using a serial friction machine (SMT-2, Russia) based on the “shaft-bushing” friction scheme, under 0.45 MPa pressure with a sliding speed of 0.39 m/s. The supramolecular structure of the polymer composites was analyzed by scanning electron microscopy (SEM) using a JEOL JXA-50 system.

RESULTS AND DISCUSSION

The physicochemical properties of PTFE and its composite containing 2% of F4-NTD-2 following different ultrasonication times are presented in Fig. 1. As seen in the figure, the maximum tensile strength and relative elongation are achieved with ultrasonication for 20 min.

A recent investigation by Mashkov *et al.* showed that ultrasonication for 30 s during the processing of PTFE and

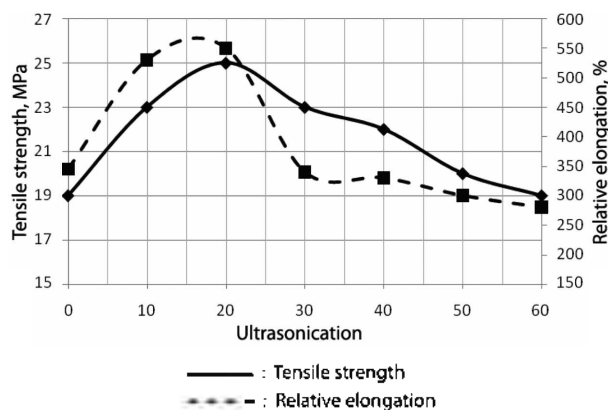


Figure 1. Effect of ultrasonication on the tensile strength and relative elongation of a PTFE composite containing F4-NTD-2.

its graphite composites increased the tensile strength by up to 10%, but decreased the relative elongation and mass wear rate to 8% and 27%, respectively.¹⁷ Because polymer processing generally occurs for less than 1 min, ultrasonication would not be effective for time durations longer than 1 min. Therefore, we concluded that 30 s is too short to induce changes supramolecular structure, and consequently the physicochemical properties, of the polymer and its composites. This is the main reason we conducted ultrasonication of the materials in their solid state before polymer processing occurred.

The bulk density of PTFE powder was evaluated in order to investigate changes in the properties of PTFE. The bulk density of PTFE was 0.505 g/cm^3 before ultrasonication and 0.585 g/cm^3 after ultrasonication. The 16% increase in bulk density is due to the enhancement of intermolecular interaction during ultrasonic processing.

Ultrasonication was carried out for 20 min on polymeric mixtures of PTFE with differing F4-NTD-2 contents. As shown in Fig. 2, ultrasonication of the powder forms of the PTFE/F4-NTD-2 polymeric mixtures increased the tensile strength by up to 25% (with the addition of 1% F4-NTD-2), and a 180% increase in the relative elongation was observed for the composite containing 2% F4-NTD-2 in comparison with the unadulterated PTFE.

We speculate that ultrasonication activates polymer chains and increases their mobility, allowing them to form a crystalline structure like that of spherulite. This reorganization of the polymer chains leads to improved physicochemical and tribotechnical properties, such as tensile strength, relative elongation, and wear resistance.

Ultrasonication of PTFE/zeolite composites was investigated in order to evaluate any change in wear resistance. A mechanically activated zeolite²² was treated with sodium stearate as the surface activating substance (SAS),²⁶ and then ultrasonicated for 10 min to promote deagglomeration.²⁷ The resulting mixture was combined with PTFE and ultrasonicated for 20 min. The changes in the physicochemical and tribotechnical characteristics of the PTFE composites induced by ultrasonication are summarized in Table 1.

As is evident from Table 1, PTFE shows high relative elongation and tensile strength, but its high mass wear

Table 1. Property changes in PTFE/zeolite composites after ultrasonication

No	Composition	Tensile strength σ_p , MPa	Relative elongation, ϵ_p , %	Mass wear rate I, mg/h
1	PTFE	24–25	460–470	70–75
2	PTFE+1 wt% zeolite	21–22	340–350	3–4
3	PTFE+2 wt% zeolite	18–19	460–470	0.6–0.7
4	PTFE+5 wt% zeolite	16–18	370–390	1.2–1.4

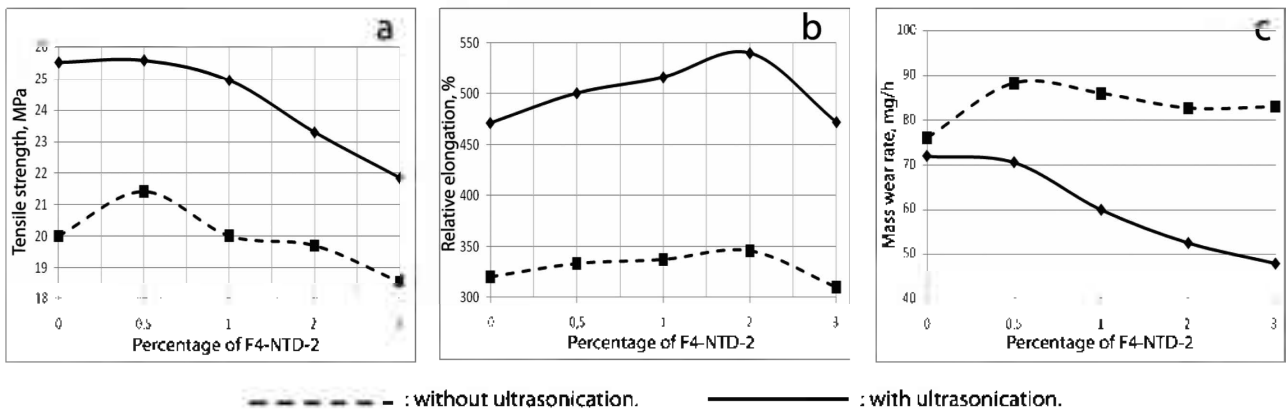


Figure 2. (a) Tensile strength. (b) relative elongation, and (c) mass wear rate of PTFE/F4-NTD-2 polymeric mixtures.

makes it unsuitable for applications under severe loading conditions. The maximum enhancement in the desired properties is seen in the PTFE composite containing 2 wt% zeolite. This composite exhibits high relative elongation and a very low mass wear resistance. The small decrease observed in the tensile strength for this material is acceptable when one considers the significant improvements in its other properties. Investigations into the size distribution of the zeolite reveal that the number of smaller particles increases after ultrasonication. This observation can be explained by the ultrasonic deagglomeration of the zeolite.²⁸

We speculate that the polar carboxylate groups of the fatty acids in the SAS interact through hydrogen bonding with the surface of the fine zeolite particles to form micelle monolayers, as shown in Fig. 3. Then, during the dry mixing process and subsequent ultrasonication, the hydrocarbon chains of the SAS interact with PTFE through Van der Waals forces to form the composites.

As seen in Table 2, PTFE composed of only F-4NTD-2 shows an increased relative elongation but does not show any significant improvement in the mass wear rate. PTFE with a 2% zeolite content shows a small decrease in the tensile strength and a significant decrease in the mass wear rate, which are the most important characteristics for applications under high-stress conditions. Addition of 2% F-4NTD-2 as a

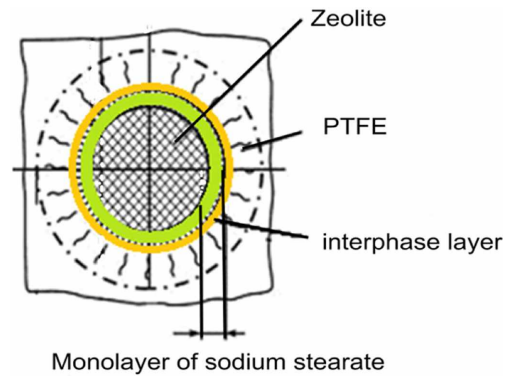


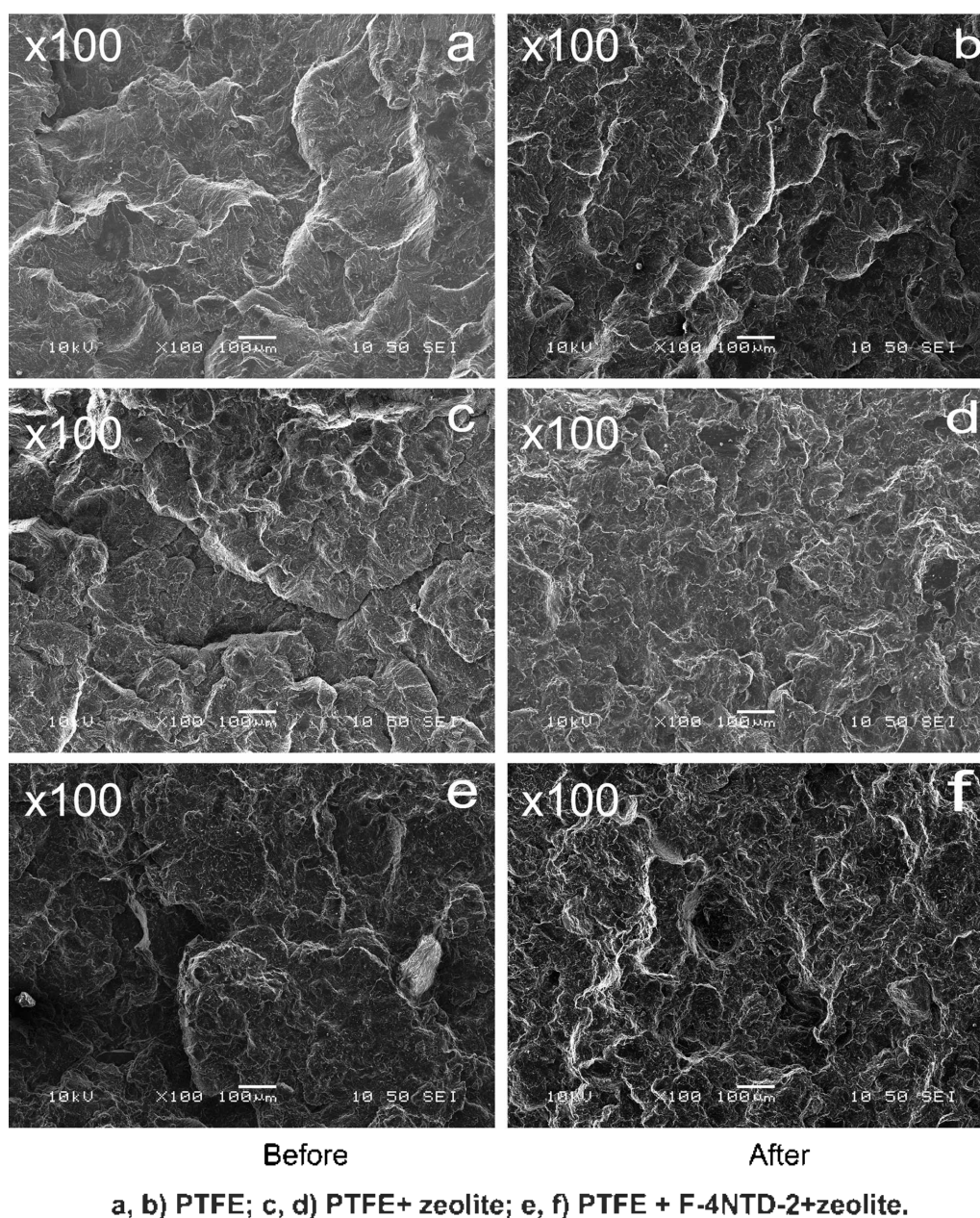
Figure 3. A possible structure of the PTFE-SAS-zeolite composite.

plasticizer to the PTFE + 2% zeolite composite does not cause any notable improvement in the tensile strength and mass wear rate as compared to the case of the PTFE + 2% zeolite composite. Therefore, we can conclude that F-4NTD-2 is not necessary for practical applications, and that the composite of PTFE containing 2% zeolite displays the most optimized tribotechnical properties for severely stressful applications.

The supramolecular structures of PTFE and its composites before and after ultrasonication were investigated by SEM. Before ultrasonication, lamellar structural characteristics are observed in PTFE, as shown in Fig. 4a. After ultrasonication,

Table 2. Property changes in PTFE composites by ultrasonication

Composition	Tensile strength σ_p , MPa	Relative elongation, ϵ_p , %	Mass wear rate I, mg/h
PTFE (before ultrasonication)	19–20	300–320	70–75
PTFE	24–25	460–470	70–75
PTFE + 2 wt% F-4NTD-2	23–24	540–550	50–55
PTFE + 2 wt% zeolite	18–19	460–470	0.6–0.7
PTFE + 2 wt% F-4NTD-2 + 2 wt% zeolite	14–15	520–530	1.2–1.7



a, b) PTFE; c, d) PTFE+ zeolite; e, f) PTFE + F-4NTD-2+zeolite.

Figure 4. SEM images showing the supramolecular structure of PTFE composites before and after ultrasonication.

more dominant fine lamellar and spherulite structure characteristics are observed, as shown in *Fig. 4b*. In the PTFE/zeolite composite, before ultrasonication, lamellar characteristics are not present, but spherulite structures are observed, as shown in *Fig. 4c*. After ultrasonication, smaller and numerous spherulite-type structures are observed, as shown in *Fig. 4d*. It is apparent from these results that zeolite acts as a crystallization center to form a spherulite. When F-4NTD-2 as a plasticizer is added to the PTFE/zeolite composite, spherulite structures are observed, as in the case of the PTFE/

zeolite composite. However, several black cavities are also observed, both before and after ultrasonication, as shown in *Figs. 4e* and *4f*. We speculate that these cavities result from the fact that F-4NTD-2 has a lower thermal expansion coefficient than PTFE, and that this difference manifests after the composite is processed at 375 °C.^{18,19} Although the presence of F-4NTD-2 in the PTFE/zeolite composite increases the relative elongation slightly, it also decreases tensile strength and wear resistance as compared to the unplasticized PTFE/zeolite composite.

CONCLUSIONS

Ultrasonication of PTFE and its zeolite composites before processing activates the polymer chains and increases their mobility, resulting in a change in the supramolecular structure. After ultrasonication, these materials exhibit enhanced spherulite crystalline properties, which in turn results in changes in the physicomechanical properties such as tensile strength, relative elongation, and wear resistance. The optimum physicomechanical properties for applications under severe climatic conditions were observed in PTFE containing 2% zeolite. Addition of F-4NTD-2 to the PTFE/zeolite composite did not convey any significant improvements, so this additive is not considered to be of any value for practical applications.

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