

## Solid-State Recycling of Polyimide Film Waste

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**ABSTRACT:** Possibility of the polyimide (PI) films waste recycling by solid-state mechanochemistry was investigated in this study. Obtained PI powder was used for development of thermostable blends and multicomponent tribocompositions, which include additions of carbon black, ultradispersive diamond powder, and quasicrystals. PI films waste treatment was provided in high-energy planetary ball mill. Powder compositions were mixed by low-energy planetary ball mill. Bulk samples were obtained by compression molding. Structural and thermal properties of initial polymers and composite materials were determined from scanning electron microscope, differential scanning calorimetry, thermogravimetric analysis, dynamic mechanical analysis and fourier transform infrared spectroscopy. Tribological tests of composite materials were provided in dry sliding regime on "pin-on-disk" tribometer. Finally, optimal regimes of polymer composite materials producing were obtained. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** polyimide; waste recycling; mechanochemistry; planetary ball mill; compression molding; thermostability; wear resistance

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### INTRODUCTION

Utilization of the plastic waste and search for solutions for its secondary usage are actual problems of today. First of all, that is explained by a growing environmental pollution, as result of a manufacturing of the primary synthetic polymeric raw, and impetuous expansion areas of polymeric waste, whose degradation period too long in natural conditions. Effective usage of accumulated waste would allow to reduce a consuming raw. High performance polymers waste is especially costly for its recycling and secondary using. This category includes a polyimide (PI) films waste, which possesses high thermostability, chemical properties, and wears resistance.<sup>1</sup> There are two main ideas about using PI powder obtained from films waste. The first idea is the development of a composite materials based on PI matrix, where the main problems are powder compactability, sinterability promotion, and optimal molding parameters researching. The second idea is the development of multicomponent polymeric composite materials with improved melt flowing or elasticity.

The main goal of this study is to determine the availability of solid-state mechanochemistry for the PI films waste recycling and development of the thermostable tribocomposites.

### THEORETICAL PART

PI's are a class of high performance polymers which possess excellent thermal and chemical stability and also a good

mechanical properties.<sup>2</sup> They are used in many important areas where other polymers unworkable (moving, bearing, sealing parts for extreme conditions). One of important problem in PI chemistry is a poor moldability (especially for thermoset PIs), where the molding techniques inaccessible cause a very high viscous and temperature processing. For solving this problem, it was developed with various PI trademarks which possess a good moldability with keeping a good thermal properties but not so high as thermoset PI. Another solution can be the usage of a special plasticizers as molding agents,<sup>3</sup> which decreases a glass temperature and improves PI flowability.

### High Temperature Thermostable PI Compositions

As mentioned earlier, PI composition development with excellent thermostability and moldability is important problem in PI chemistry. One of the ways of the melt rheology improvement is the development of the polymeric compositions injectability,<sup>4–7</sup> such as PI/polyphenylene sulfide (PPS), for example. PPS is a high performance thermoplastic polymer which possess excellent melt flowing. Another interesting direction is the development of polymeric compositions with improved elasticity and impact-resistance such as PI/polytetrafluoroethylene (PTFE)<sup>8,9</sup> or PI/elastomer.<sup>10</sup> In addition, there are some interesting examples of using a PI powder in the multicomponent compositions,<sup>11–17</sup> where it has significant improvements of wear resistance as a result of combination effects of two or more additions. Thus, it

has been suggested that PI addition would be a very effective in combination with other fillers. Compositions preparation details and their properties (thermal, mechanical, tribological) can be found in patents and only a conclusions of review follow next.

In mechanical formation, a binary polymeric systems like PPS/PI (where PI in dispersion state) a mechanical behavior of that composite comparable with metallic, ceramic or other dispersion filled polymeric composites: increasing of the PI concentration improves elastic properties and decreases strength properties and elasticity. Meanwhile in a number of patents a significant improving wear resistance is noticed. In some patents, a heat distortion temperature increasing, decreasing coefficient of expansion, and etc., are reported. But, these effects are often obtained in composites where metallic, ceramic, and other fillers are used and their cost can be less in many cases. Thereby, it would be interesting to obtain some kind of polymeric composition where PI will have a sintering state.

#### Solid-State Mechanochemistry as One of the Utilization Technique of Polymeric Waste and Development Polymeric Composition

Solid-state mechanochemistry consists of the PI films waste treatment by planetary or vibration ball mills. Mechanical treatment leads to structurization and activation processes in particles' surface layer. These processes allow to improve a compactability and sinterability of final PI powder. Mechanochemical treatment is a nontraditional-polymer technique, though the one of the first researching work in solid-state mechanochemistry of polymers was presented a long time ago.<sup>18</sup> Systematic researches have started at the early 1990s,<sup>19–21</sup> and by the early of the 2000s, a number of publications has increased significantly.<sup>22–30</sup> This researches discovered a changes during a polymer solid-state treatment which include: particle size dispersion and average size, powder morphology, molecular weight dispersion and average value, structure (crystallinity, phase transitions), thermal properties (points of melting, glass, crystallization, enthalpy of transitions, and etc.), and mechanical properties. In addition, some aspects of polymeric composite materials were investigated which include: evolution of composite material structure formation, surface energy components evolution, influence of the treatment duration at filler dispersion, and its comparison with a melting mixing techniques like extrusion. The main process during mechanochemical treatment polymers that obtained in many researches is decreasing an average molecular weight and structure amorphization. The first occurrence is irreversible and second occurrence is restorable with following thermal treatment that included in polymer melting. In addition, it was discovered that mechanochemical treatment of the polymers with a hard fillers leads to acceleration of grinding. Also, it was showed that mechanochemistry prevents filler agglomeration and final powder mixtures are more uniform in comparing with a melting mixing technique like extrusion.

#### EXPERIMENTAL PART

##### Development of the Solid-State Treatment Method for the Kapton PI Film Waste Recycling

Solid-state treatment of a PI films waste took place in the high-energy planetary mill MPF-1 (Figure 1). Working parameters of



Figure 1. High-energy planetary ball mill MPF-1.

the high energy planetary mill MPF-1 are summarized in Table I. This type of mill has a large energy transfer and consequently a high grinding efficiency in a short time period. As alternative solution a rotary mill Fritsch Pulverisette 14 and planetary ball mill Fritsch Pulverisette 5 were considered. In first case, raw films tends to concentrate in top (or dead zone) of rotor and treated material seems to be ungrinding. In second case, Fritsch Pulverisette 5 is less preferable than MPF-1 when we work with viscoelastic materials such as polymers. But, Fritsch Pulverisette 5 is a good solution for making powder compositions.

Contaminants in powder compositions were objected by X-ray diffraction and fluorescence assay after mechanochemical treatment in MPF-1. It was the result of a PI films grinding – milling bodies wear steel from ball's/vial's wall. Therefore, it has been performed a methodological research for minimization this undesirable effect and increasing a grinding efficiency (working parameters for each case see in the Table I).

Pictures of initial chopped PI film and PI powders with various iron contamination are illustrated in Figure 2.

Figure 3 shows the scanning electron microscope (SEM) micrographs of the powders marks "1" and "4" at various magnification. In case powder "1" average particle size  $\sim 100 \mu\text{m}$  and thickness  $\sim 10 \mu\text{m}$ . In some areas, large particles  $\sim 200 \mu\text{m}$  and small inclusions of ferrum particles are also discovered. In case powder "4," average particle size is  $\sim 30 \mu\text{m}$ . However, powder "4" is more homogeneous than powder "1." PI powders "1" and "4" were used for making powder compositions.

From differential scanning calorimetry (DSC) and thermogravimetric analysis (TG), it was obtained that glass temperature  $\sim 360 \text{ }^\circ\text{C}$  and melting temperature does not exist (Figure 4). The point of thermal degradation is  $\sim 450 \text{ }^\circ\text{C}$  for the PI powder and  $\sim 500 \text{ }^\circ\text{C}$  for initial film.

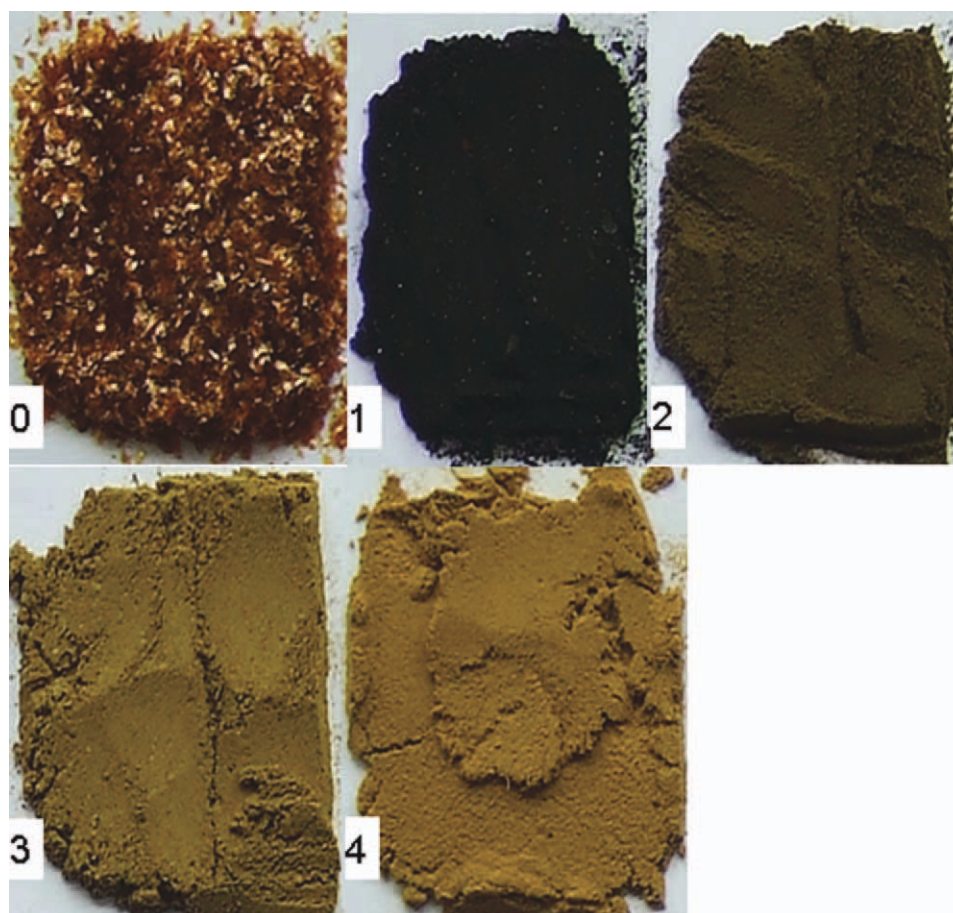
To confirm structural changes of PI after mechanochemical treatment, FTIR (Fourier transform infrared spectroscopy) of neat PI film Kapton and PI powder was performed by a Nicolet 380 spectrometer. The IR spectrums were recorded over the range  $650\text{--}2000 \text{ cm}^{-1}$  and the results are shown in Figure 5.

**Table I.** High-Energy Planetary Ball Mill MPF-1 Working Parameters

Sample (polyimide film)	1 (1a)	2	3	4
Motor velocity (rpm)	900			
Vial material	Hardened steel			
Vial volume (ml)	373			
Ball material	Steel 100Cr6			
Ball diameter (mm)	6-10	7; 8	7; 8.73	7; 8.73
Ball number ratio (pcs.)	-	288/198	274/140	274/140
Ball loading (g)	970	822	768	768
Powder mass loading (g)	50 (25)	20	45	45
Degree of the vial filling (%)	54	45	43	43
Weight ratio (balls/powder)	20/1 (39/1)	41/1	17/1	17/1
Work/rest cycle (min)	3/5			
Treatment duration (min)	60 (85)	60	87	89
Cooling system	Water			

The main peaks of PI Kapton observed from IR spectrum and their brief characterization are summarized in Table II. Illustration of the chemical structure of PI Kapton is shown in Figure 6.

As follows from Figure 5, structure of the Kapton PI is undergoing significant changes after milling in MPF-1 planetary ball mill. Intensity of the major IR peaks increases that may associate with processes of PI oxidation. It is explained by breaking of



**Figure 2.** Initial PI film and PI powder. 0: chopped initial PI film, 1–4: PI powder after milling in planetary ball mill MPF-1 (iron contamination reduction). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]



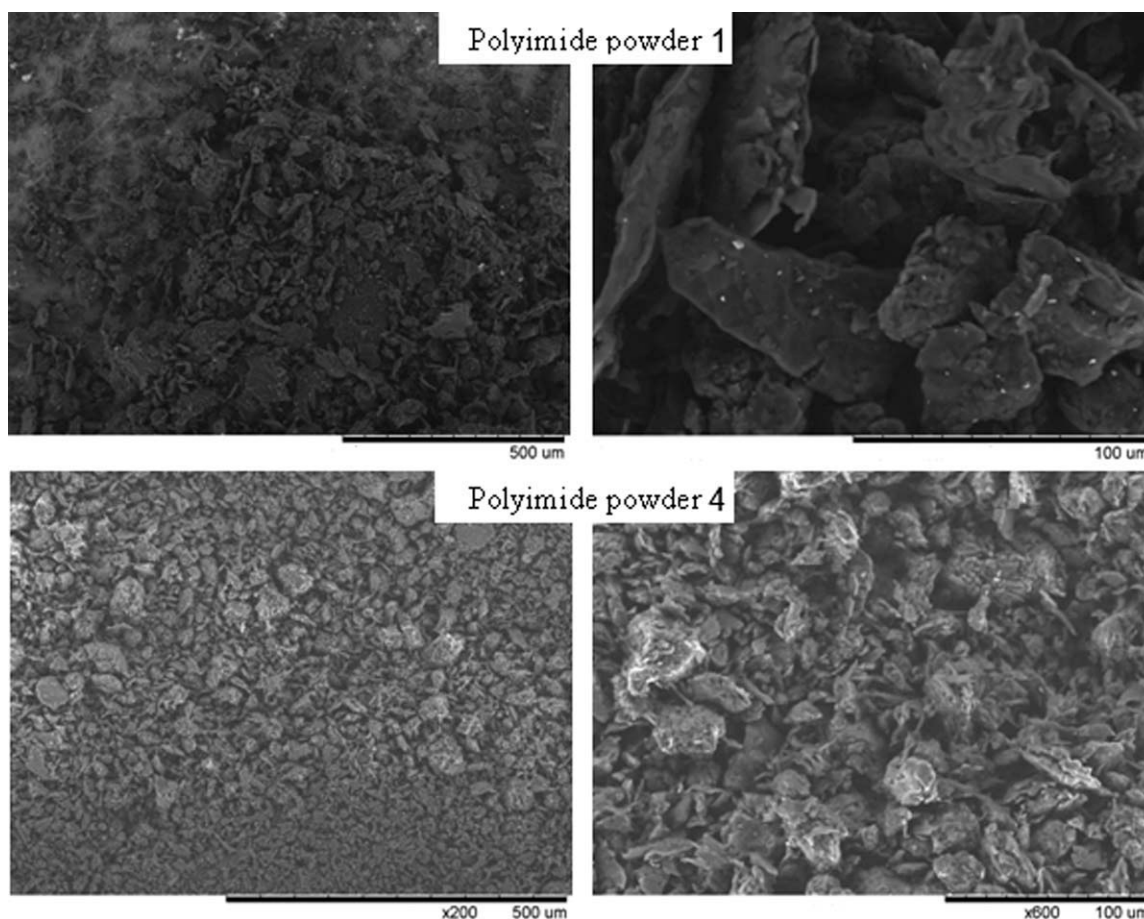


Figure 3. SEM images of the PI powders “1” and “4” at various magnifications.

the PI macromolecules which leads to the active radicals formation,<sup>33</sup> and correspondingly, considerable hydrophilization of the PI, as detected by the goniometric method.<sup>34</sup>

In this article,<sup>35</sup> it is reported that amorphization or crystallization processes can be estimated from changing in the amorphous-responsive bands ( $726$  and  $885\text{ cm}^{-1}$ ) optical density and crystal-responsive

band ( $800\text{ cm}^{-1}$ ). As follows from IR spectra, intensity of amorphous-responsive bands increases while crystal-responsive band is not found. This evolution of the IR spectra can indicate that PI structure undergo an additional amorphization during ball milling.

Thereby, a principal possibility of high dispersion PI powder preparation from film waste using high energy ball milling was

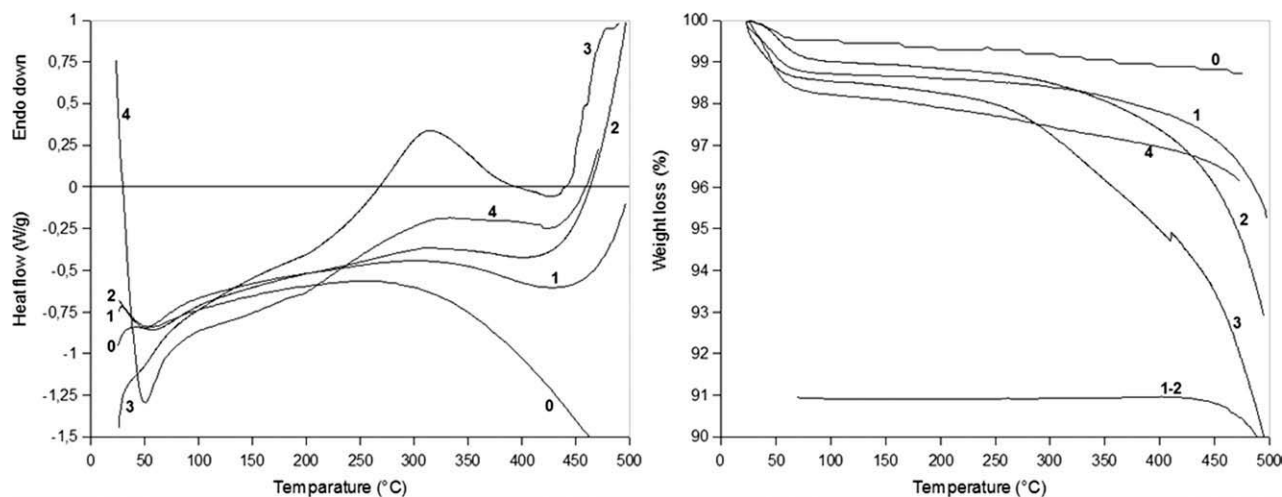
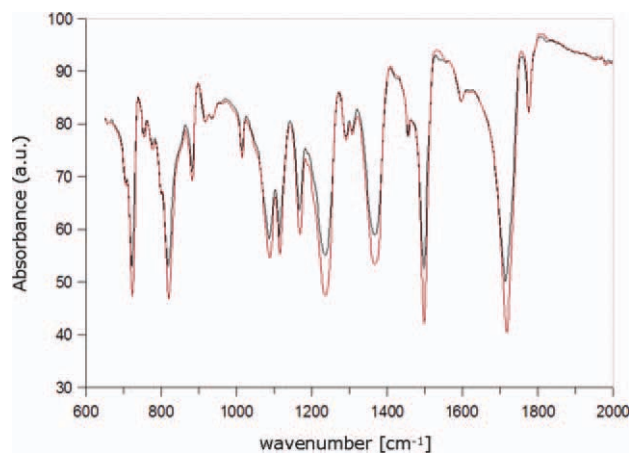


Figure 4. DSC-TG curves of the initial PI film and PI powder. 0: initial PI film, 1–3: PI powder “1,” and 4: PI powder “4.”



**Figure 5.** IR spectrum of virgin PI film Kapton (black line) and PI powder obtained by mechanochemical treatment in high energy ball mill (red line). [Color figure can be viewed in the online issue, which is available at [www.onlinelibrary.com](http://www.onlinelibrary.com)]

demonstrated. It must be noticed that grinding efficiency for polymeric materials depends on their viscoelastic properties and working parameters (energy transfer, temperature, and etc.). In case of viscous polymers recycling (high-density polyethylene, PTFE, e.g.) grinding efficiency would be low at high level of energy transfer. But, it would be significantly higher at cryogenic temperature (i.e., lower polymer glass temperature where it becomes brittleness). However, these arrangements also lead to increasing of technology's price.

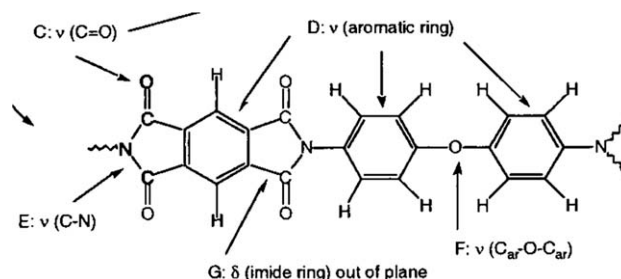
### Tribological Tests of Polymer Composite Materials Contained Recycled PI

Binary systems F-4MB(fluorinated ethylene propylene)/PI and PPS/PI in concentration range 0–75 wt % of the PI, ternary compositions and multicomponent composition which include additions of carbon black (CB), quasicrystals Al–Cu–Fe (QC) and nanodiamonds (ND) composition of the investigated samples are given in Table III.

Powder compositions were obtained by solid-state treatment in planetary mill Fritch Pulverizette 5. Bulk samples for mechanical

**Table II.** The Major Peaks of PI Kapton Observed from IR Spectrum

Peaks	Assignment <sup>31</sup>	Characterization <sup>31</sup>
721	$\delta(\text{C-N-C})$	Imide deformation
818	$\delta(\text{C-H})$	Out-of-plane phenyl deformation
881	$\delta(\text{phenyl})$	Phenyl ring deformation
1013		
1086		
1113	$\nu(\text{C-N-C})$	Imide stretch
1167	$\nu(\text{C-N-C})$	Imide stretch
1245	$\nu(\text{C}_{\text{ar}}-\text{O}-\text{C}_{\text{ar}})$	Bridging $\text{C}_{\text{ar}}-\text{O}-\text{C}_{\text{ar}}$ stretch
1365	$\nu(\text{C-N-C})$	Imide stretch
1497	$\nu(\text{phenyl ring})$	Phenyl ring C–C stretch
1713	$\nu(\text{C=O})$	Out-of-phase carbonyl stretch
1775	$\nu(\text{C=O})$	In-phase carbonyl stretch



**Figure 6.** Chemical structure of the Kapton PI film (32).

and tribological tests were received by compression molding. Various regimes of compression molding are illustrated in Figure 7 (heating rate  $\sim 3\text{ }^\circ\text{C}/\text{min}$ , cooling rate  $\sim 4\text{ }^\circ\text{C}/\text{min}$ ). Step by step pressure loading was used for prevention of material outflowing from steel mold. After final step, pressure loading was hold until 150–170  $^\circ\text{C}$  in cooling process. Pressure was rejected and samples were removed at 70–80  $^\circ\text{C}$ .

Tribological tests were conducted in a dry sliding regime at complex parameters that simulate the behavior of sealing and bearing units of a broad machinery class.<sup>36</sup> There was used friction model “pin-on-disc” (Figure 8). Steel disk had 55 Rockwell hardness at scale C and average roughness 0.2  $\mu\text{m}$  (9 class). Load 19 N, sliding velocity 2.5 m/s, sliding distance ( $L_d$ ) 4.6 km for each test.

For coefficient of friction and wear intensity calculation following formulas were used:

$$f = (2 \cdot M) / (D \cdot F_N) \quad (1)$$

$f$  – coefficient of friction;  $M$  – friction moment, kg/cm.

$$I = h / L_d \quad (2)$$

$I$  – wear intensity, mm/mm;  $h$  – height wear track, mm.

## RESULTS AND DISCUSSION

Study of the binary system F-4MB/PI in concentration range 0...75 wt % PI showed that effect of single PI addition has almost no influence on friction (Figure 9), but wear decreases two times at 50 wt % PI. It was also noticed that hardness and elastic modulus increase, but higher PI concentrations lead to significant brittleness of composite material.

**Table III.** Polymer Composite Materials Contained Recycled PI

Composition	wt %
F-4MB/PI	75/25; 50/50; 75/25
F-4MB/PI/CB	75/20/5
F-4MB/PI/CB/QC Al–Cu–Fe	10,8/2,5/1,2
PPS/PI	75/25; 50/50; 75/25
PPS/PI/CB	50/35/15
PPS/PI/F-4MB	35/50/15
PPS/PI/ND	49,75/49,75/0,5

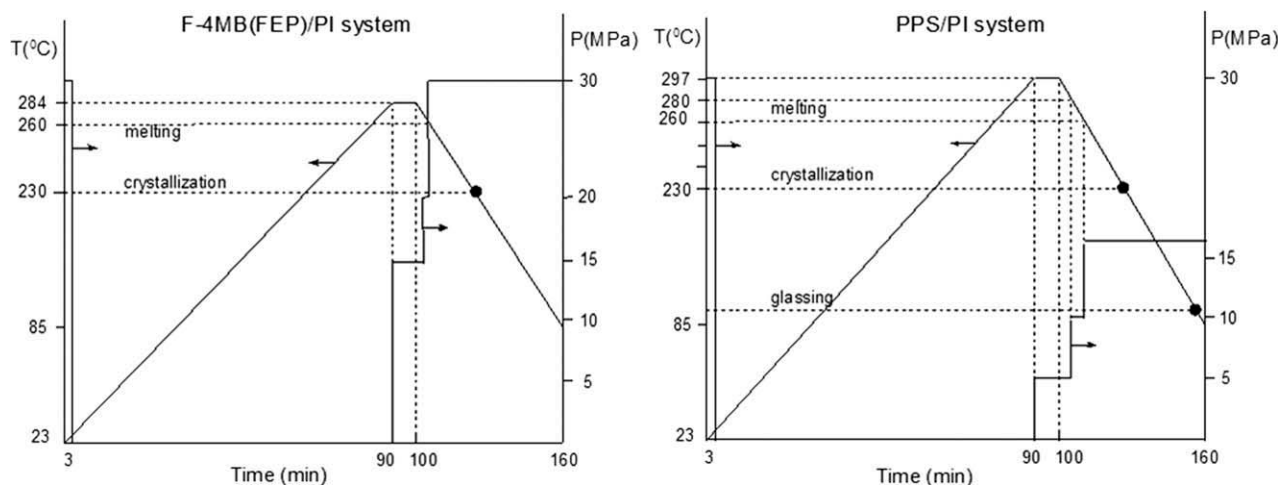


Figure 7. Molding regimes.

For keeping useful properties of the F-4MB, it has been decided to limit concentration range from 0 to 25 wt % PI (Figure 10). CB was chosen because of high surface activity, which can

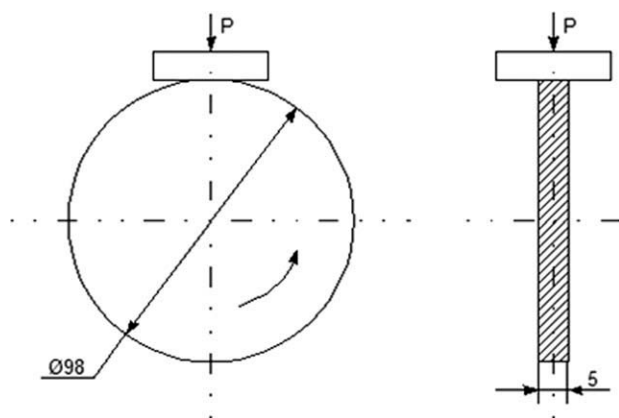


Figure 8. Friction model "pin-on-disk."

promote interaction between components and improve anti-friction composite performance. However, following experiments have showed that wear and friction coefficient of the F-4MB/PI/CB and F-4MB/CB systems almost the same, although hardness and elastic modulus are higher for ternary compositions. QC have a high hardness and low coefficient of friction.<sup>37</sup> However, binary system F-4MB/QC has showed a low efficiency of QC addition on wear of composite material. That can be explained by their low surface activity. QC particles can be easily chipped from the polymer matrix during friction process.

Multicomponent system F-4MB/PI/CB/QC has showed increase of wear resistance and decrease of the friction coefficient in comparing with unfilled F-4MB and others tested compositions based on F-4MB. For explaining this result, it was the suggested "multiscale structure" model of composite material (Figure 11). The idea is that PI particles have flake morphology and they cover small QC particles. Thus, the QC filler decreases wear of composite material.

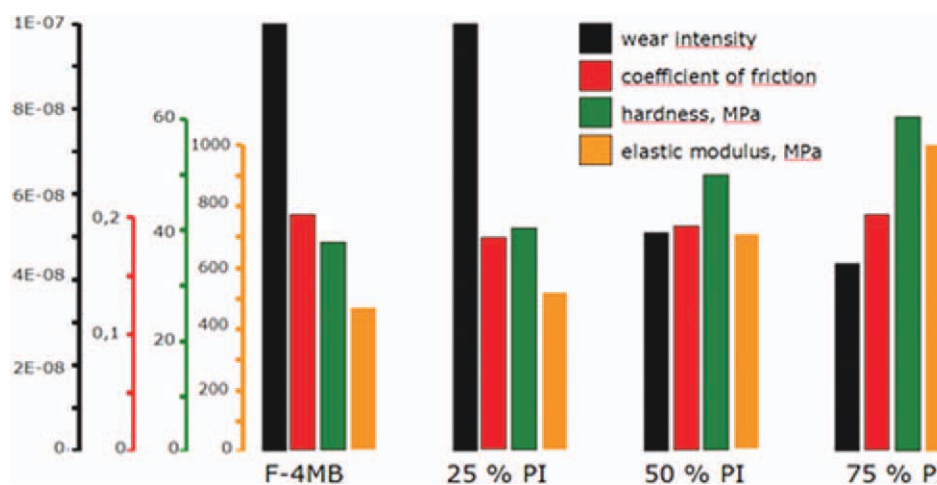


Figure 9. Tribotesting results for binary system F-4MB/PI. Test conditions: steel ball diameter 9.6 mm, load 71 N, and time loading 1.5 min. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

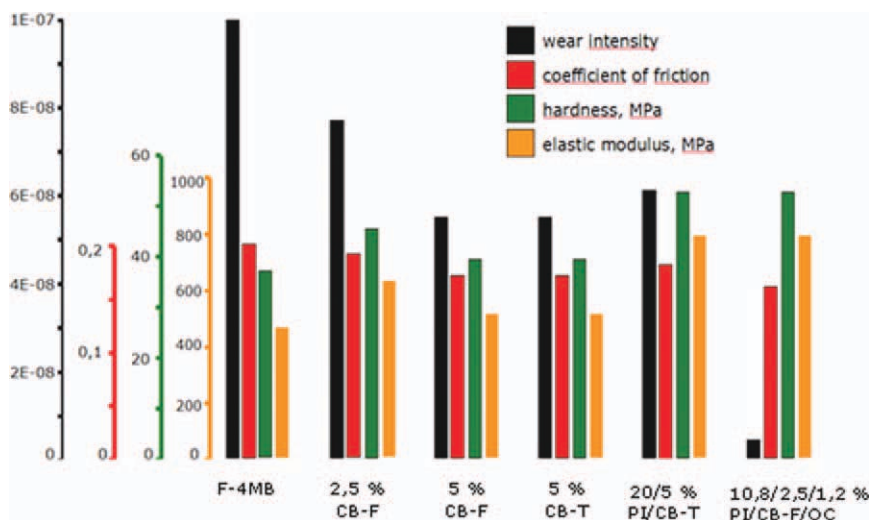


Figure 10. Tribotesting results for multicomponent system based on F-4 MB (CB: T – thermal and F – furnace). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

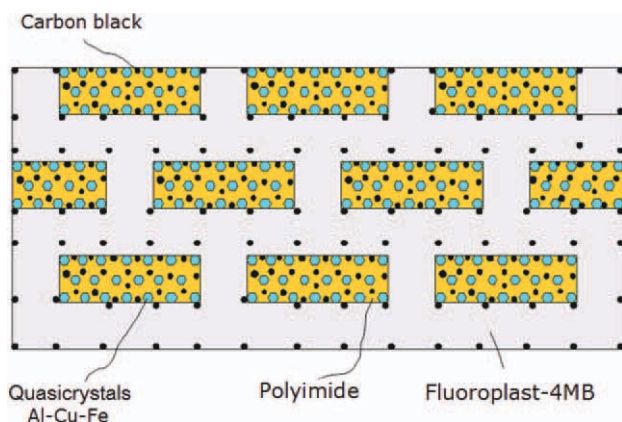


Figure 11. "Multiscale structure" composite model. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

Study of the binary system PPS/PI in concentration range 0–75 wt %, PI showed that influence of a single PI addition has decreased wear intensity in order with some decreasing of hardness and elastic modulus, but friction coefficient has stayed almost the same (Figure 12). Dispersion and homogeneous of PI powder have a significant influence on tribological performance of composite material: with decreasing of average powder size their action efficiency on decreasing wear improved in three to four times, but friction coefficient increases slightly. In addition, filling until 50 wt % PI has not led to the composite brittleness as in case of F-4MB/PI system that can indicate a good binding ability of the PPS or good interface adhesion. This considerations were confirmed by the results of DSC and dynamic mechanical analysis. For improving of PPS/PI system sliding performance, it was obtained ternary compositions with CB, F-4MB, and ND additions (Figure 13). Results of test have

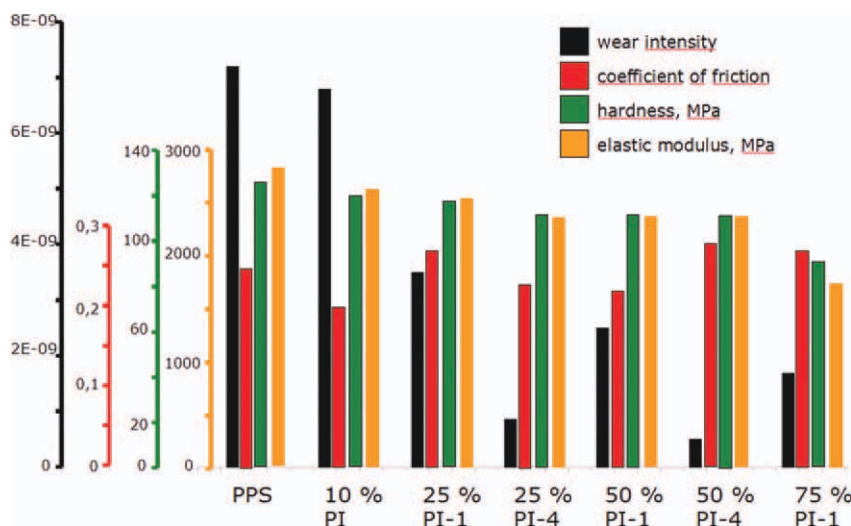
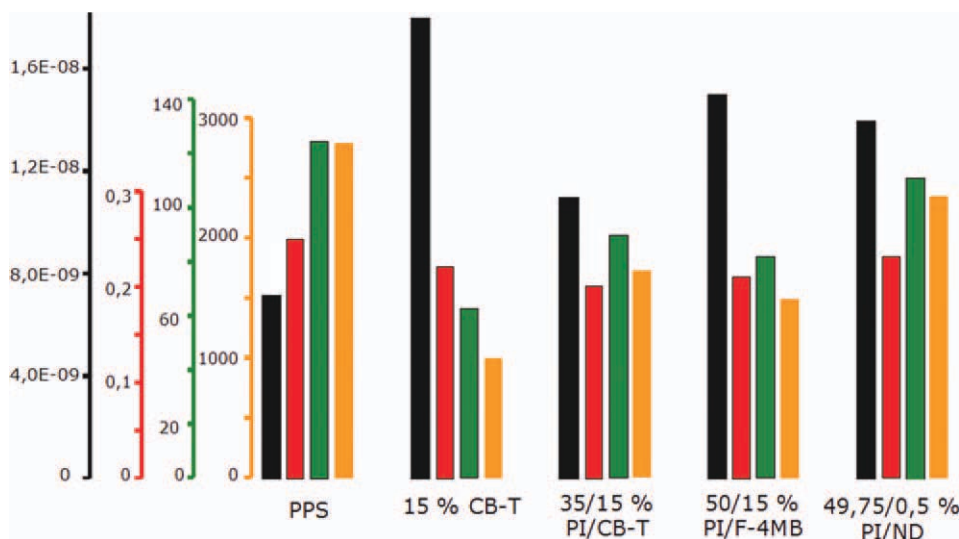


Figure 12. Tribotesting results for binary system PPS/PI. PI powder: dispersion marks "1" and "4" (see pt. 2.1). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]





**Figure 13.** Tribotesting results for multicomponent system based on PPS. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

showed that addition 15 wt % CB leads to significant loss of composite strength which reflected in decreasing of hardness and elastic modulus. It can be explained by high concentration of CB which leads to formation of weaken structural network between particles. In ternary system, 35 wt % PI was shown as the hardness and elastic modulus decreasing without changing the tribological properties. It has been suggested that improvement expected at less CB concentrations. In addition 15 wt % F-4MB indicates decreasing of hardness, elastic modulus, and increasing wear intensity.

It is believed that significant improvements of tribological properties can be reached by optimization of molding regimes. Introduction of a small amount of ND into PPS/PI system also does not lead to improvement of tribological properties of the composite materials. On the contrary, ND filler leads to intense abrasive wear during friction process. Thus, under the given composition concentration a ternary systems are worse than binary systems PPS/PI in tribological properties.

## CONCLUSIONS

1. The PI film waste recycling method using high-energy planetary ball mill was developed. After mechanochemical treatment, PI powder with average particle size 30  $\mu\text{m}$  can be received.
2. Efficiency of single PI addition on tribological properties of composite materials depends on powder dispersion of the PI and structure of the composite:
  - decreasing a size of the PI powder improves wear resistant;
  - PI does not effect on system fluoroplast/PI;
  - PI addition decreases wear in order in system PPS/PI.
3. Multicomponent composite F-4MB/PI/CB/QC has higher wear resistance and low friction coefficient as compared with binary systems F-4MB/ -PI, -CB, -QC and ternary system F-4MB/PI/CB.

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