# Synergistic effect of $Ni_2O_3$ on flame retardancy of thermoplastic polyurethane intumescent flame retardant system

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## Abstract

**The aim of this work was to study the effect of nickel trioxide ($Ni_2O_3$) on TPU intumescent flame retardant system. The flame retardancy performance was examined through the analysis of the limiting oxygen index (LOI) and the SEM microstructure observation of brittle-fractured surface and residual char layer after complete burning. Results show that a certain amount of $Ni_2O_3$ can provide synergistic effect, including increase in the LOI value and yield of the residual char and improvement in the quality of char layer. But excess amounts of $Ni_2O_3$ can destroy the density of char layer and lead to a decline in the flame retardancy of the composite.**

## Keywords

**Thermoplastic polyurethane; intumescent flame retardant; synergistic effect; $Ni_2O_3$.**

## 1. Introduction

As the society and materials related industry progress, people pay further attention on the environmental issues and more countries implement various environmental policies, such as the EU RoHS directive. The use of lead, mercury, cadmium, hexavalent chromium, polybrominated diphenyl ethers (PBDE), polybrominated biphenyl (PBB), and some other hazardous substances have been prohibited in electrical devices supplied to the market from July 1, 2006. Japan's electronics industries have formulated the corresponding requirements that all kinds of wires and cables used in electrical devices must be non-halogenated since March 2006. Thus, halogen-containing flame retardant products have gradually been withdrawn from the market, and more people were attracted to study new halogen-free flame retardant polymers.

Thermoplastic polyurethane (TPU) is a kind of elastomer with excellent properties, including high wear resistance, oil resistance, transparency, and hardness. It can be widely used as automotive parts, shoes sole, rubber roller, wire and cable, hose, sheet, film, and fabric (layer and highly elastic socks) [1]. Polyurethane has excellent properties and has been widely used but its poor flame retardancy restricts applications. The limiting oxygen index (LOI) value of PU is only approximately 20%, it drops easily in fire and continues to burn, producing large amounts of smoke with strong smell. These disadvantages restrict its use, therefore, flame retardancy modification is necessary when TPU is used in wire and cable industry[2].

At present, intumescent flame retardant is widely used in TPU halogen-free flame retardant system. For example, Hao et al[3]added ammonium polyphosphate (APP) to TPU after being microencapsulated by melamine resin and found that the UL-94 vertical burning rating reached FV-0 and LOI value reached 35% as the total amount of flame retardant was 35%. Chen et al[4] microencapsulated APP with hydroxyl silicone oil and compared the flame retardancy and water resistance of microencapsulated TPU with that of untreated TPU. The study revealed that when 20% of APP microcapsules was added, a vertical burning rate was achieved with V-0 rating. In addition, at the same amount of additive, the LOI value and water resistance of APP microcapsule flame retardant material were also better than untreated APP flame retardant materials. Zhao et al[5] modified TPU with microcapsulated ammonium polyphosphate (MAPP) and boron phosphate (BP) and observed that the flame retardant material can reach V-1 rating in vertical burning examination when the additives included15.5% MAPP and 2% BP. Microcapsulated APP can improve the APP compatibility with the TPU matrix, enabling it to uniformly disperse in the matrix and greatly improve the flame retardant performance of the polymer.

Yu et al[6,7] studied the effects of $Ni_2O_3$ on combustion of polyethylene, polypropylene and other nonpolar polymers and observed obvious catalytic effect of $Ni_2O_3$ on polyolefins carbonation. For example, addition of $Ni_2O_3$ to PP increased the yield of residual char. When the amount of $Ni_2O_3$ was 5%, the residual char yield increased from 0% to 14% at 700 ℃ and the peak heat release rate decreased from 1283 to 531 KW/m2. When salts and carbon materials were added, further carbon effect was observed. For example, in the study of flame-retardant modification of LLDPE with multiwall carbon nanotubes (MWCNTs) and $Ni_2O_3$, when 3% MWCNTs and 5% $Ni_2O_3$ were added, the residual char increased from 0% to 13.7% and the peak heat release rate decreased from 1135 to 312 $KW/m^2$.

This article mainly focuses on the synergistic effect of nickel oxide in intumescent flame retardant system. We used a kind of commercial intumescent flame retardant (IFR) and added a small amount of $Ni_2O_3$ as the flame retardant synergistic agent. These substances were added to polyether TPU and the synergistic effect of flame retardant with $Ni_2O_3$ and IFR was investigated. Through the examinations, such as the limiting oxygen index (LOI), vertical burning level, scanning electron microscopy (SEM), and mechanical property, the influence of $Ni_2O_3$ on TPU/IFR flame retardant and mechanical properties were explored.

## 2. Experimental Procedure

### 2.1 Materials.

Thermoplastic polyurethane was received from Yantai Wanhua Polyurethane of China. Vinyl tris(2-methoxyethoxy) silane (SG-SI 172) was purchased from, Nanjing Shuguang Chemical Corporation, China. Expansion type flame retardant (NP-430, phosphorus content 19%) was obtained from Jiangmen Topchem Technology, China. Nickel trioxide ($Ni_2O_3$) with a particle size of 250~300 nm was purchased from Shanghai Lingfeng Chemical Reagent, China.

### 2.2 Samples Preparation.

The TPU was dried at atmospheric for 3h at 90 ℃. TPU with IFR powder and $Ni_2O_3$ were mixed uniformly in a high speed mixer. Then, the mixtures were compounded using a twin-screw extruder (SHJ-20, Nanjing Jieya Extrusion Equipment, China) at 180~190 ℃. The screw rotation speed was 50 rpm. After granulation and cooling in water, granules were dried in vacuum oven at 90 ℃ for 3h. Then, the flame-retardant TPU/IFR-$Ni_2O_3$ samples were successfully prepared.

### 2.3 Characterization.

Tensile strength examination was carried out with a universal material testing machine (Z005, Zwick/Roell, Germany) with a cross-head speed of 50 mm/min. LOI test was performed using a JF-3 instrument (Nanjing Analysis Instrument, China), according to ASTM D638-2003 standard method with sample dimensions of 100 × 10 × 4.2 mm. Based on the UL-94 test of ASTM D3801-1996 standard, the vertical burning test was carried out on an AG5100A-type instrument (Zhuhai Angui Testing Instruments, China) with specimen dimensions of 130 × 13 × 4.2 mm. Thermal analysis was carried out with an analyzer (TG209F3, NETZSCH Company, Germany) by heating from 50 to 600 ℃ at a heating rate of 20 ℃/min in nitrogen atmosphere with a flow rate of 40 mL/min. Melt index (MI) examinations were carried out using an standard tester (SANS ZRZ1452, MTS, China) with a load of 2160 g at 190 ±0.2 ℃.

The morphologies of TPU composites and their residual chars were analyzed using a scanning electron microscope (SEM, XL-30ESEM, Dutch Philips Company, The Netherland). The composites were cryogenically fractured in liquid nitrogen and the chars were collected after LOI tests for microscopic studies. The SEM micrographs were obtained at an accelerating voltage of 20 kV on gold-coated specimens. The pictures of fracture surface and residues after LOI testing for TPU composites were recorded with a digital camera.

## 3. Results and discussion

### 3.1 Fire performance

Synergistic flame retardancy effect can be used to characterize quantitatively the synergistic efficiency (SE). SE is defined as “at the same amount, the ratio of the flame retardant efficiency (FRE) in synergistic system to flame retardant efficiency of only flame retardant substance”. The FRE is defined as “the increase in the LOI value (FRE = Δ (LOI)/w (P))” of flame retardant system for flame retardant elements (w (P)) per unit mass. When SE is greater than 1, the synergies began to take effect; the greater SE corresponds to larger effect[8].

As the experimental data in Table 1 show, samples without flame retardants in TPU provided a small LOI value (21.2%). After addition of IFR, the flame retardancy properties of system significantly improved. When $Ni_2O_3$ was added, the LOI value of TPU/IFR-$Ni_2O_3$ system initially increased and then decreased. When the amount of $Ni_2O_3$ was 4.5 phr, TPU/IFR-$Ni_2O_3$ system provided the best flame retardant synergism with $Ni_2O_3$; the LOI value increased from 30.0% to 34.2%, vertical burning level reached V-0 rating, and SE was observed as 1.52. The observations show that addition of 4.5 phr $Ni_2O_3$ results in a large synergistic efficiency.

Table 1. Results of fire performance for flame-retardant TPU composites

| Sample | TPU (phr) | IFR (phr) | $Ni_2O_3$ (phr) | LOI (%) | Δ LOI | w(P) (%) | EFF | SE | UL-94 (4.2 mm) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 100 | 0 | 0 | 21.2 | – | – | – | – | No |
| 2 | 100 | 45 | 0 | 30.0 | 8.8 | 5.90 | 1.49 | – | V-2 |
| 3 | 100 | 45 | 1.5 | 32.2 | 11.0 | 5.84 | 1.88 | 1.26 | V-2 |
| 4 | 100 | 45 | 3.0 | 33.4 | 12.2 | 5.78 | 2.11 | 1.42 | V-1 |
| 5 | 100 | 45 | 4.5 | 34.2 | 13.0 | 5.72 | 2.27 | 1.52 | V-0 |
| 6 | 100 | 45 | 6.0 | 32.8 | 11.6 | 5.66 | 2.05 | 1.38 | V-2 |
| 7 | 100 | 45 | 7.5 | 32.0 | 10.8 | 5.61 | 1.93 | 1.30 | V-2 |

### 3.2 Thermal degradation behavior

Figure 1 shows the thermographs of pure TPU, IFR-TPU composites, and nickel oxide synergistic flame-retardant TPU. According to the graphs, the degradation of TPU started at 350 ℃ and reached to its maximum at 390 ℃ and eventually completed at 450 ℃. The char remaining from the complete thermal degradation was measured as 5.2%. The degradation temperature for TPU/45IFR was observed at 290 ℃, which reached to its maximum at 370 ℃ and decomposition completed at 450 ℃. The residual char was determined as 15.2% for the sample containing 45 phr IFR flame retardants in pure TPU system. Interestingly, the degradation temperature of this sample decreased by 60 ℃ because the low degradation temperature of the flame retardant and its large amount that can reduce the core decomposition temperature of material. Residual char increased from 5.2% to 15.2% relative to pure TPU, an increase of 192.3% that greatly improves the residual char formation and the expansion of carbon that enhances the flame retardancy of the system.

After addition of $Ni_2O_3$, the residual char for TPU/45IFR-4.5$Ni_2O_3$ system was determined as 15.4%, where that of TPU/45IFR-7.5$Ni_2O_3$ system was 18.7%. The residual char from thermal degradation of TPU/45IFR and TPU/45IFR-4.5$Ni_2O_3$ samples did not show significant change in comparison with that of TPU/45IFR-7.5$Ni_2O_3$. The char remaining from TPU/45IFR-4.5$Ni_2O_3$ system increased by 3.3%, indicating that as the $Ni_2O_3$ was added, the residual char increased to a certain amount. But, when $Ni_2O_3$ was decomposed to NiO at elevated temperatures, TPU/45IFR-4.5$Ni_2O_3$ with 3.0% NiO content left 12.4% char. On the other hand, for TPU/45IFR-7.5$Ni_2O_3$ system containing 5.0% NiO, the residual char of system was measured as 13.7%. In comparison with the amount of residual char of TPU/45IFR, which was 15.4%, they both decreased. These results show that $Ni_2O_3$ cannot increase the residual char of the system; instead, it reduces the amount of residual char. There was a contradiction in synergistic flame retardancy of reference[6,7], indicating that $Ni_2O_3$ in nonpolar systems can catalyze formation of char and increase the amount of residual char, producing flame-retardant char layer. Our experimental results showed that $Ni_2O_3$ in TPU polar system cannot increase the amount of residual char during combustion; it may go through another mechanism to improve the flame-retardancy effect of the system. It was similar to the mechanism that was mentioned by Liu et al[9] in a combustion process in which $Ni_2O_3$ produced NiO at elevated temperatures. Catalyzed by NiO, the alkyl phosphate in the flame retardant additive system produces nickel phosphate that promotes the cross linking reaction between alkyl phosphates. In the system, further alkyl phosphate can be subjected to esterification reaction with pentaerythritol instead of being decomposed into $P_2O_5$. Cross-linked phosphate improves the density of char layer and forms more stable expandable char layer. As the amount of $Ni_2O_3$ increases, the performance of flame retardant declines. This is possibly due to increase in the number of $Ni_2O_3$ particles and their uneven distribution in the matrix.

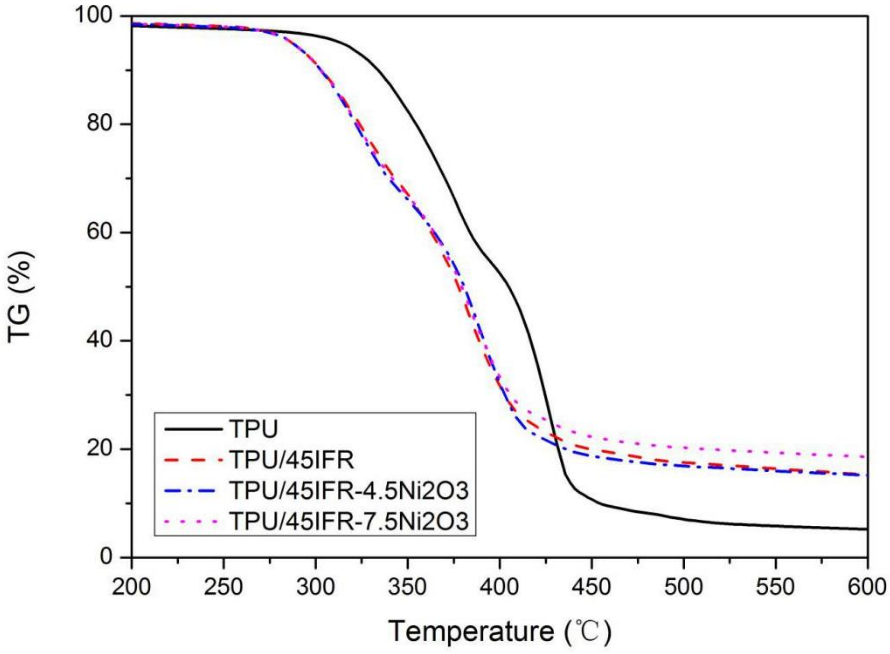

Fig. 1. TG thermograms of flame retardant TPU composites in N2 atmosphere

### 3.3 Char morphology

The microstructures of residual chars from all flame-retardant TPU composites were analyzed with SEM (Fig. 2). The char layers morphology appeared as multilayer structure with many tiny holes on the surfaces when the flame-retardant system did not contain $Ni_2O_3$ (Fig. 2a). As $Ni_2O_3$ was added, tiny holes of the char layers disappeared (Fig. 2b,c,d). Char layers appeared in uneven shape by the inert gases produced during the degradation of flame retardant additives but, compared with micrograph in Fig. 2a, their density significantly increased. The char layers became most integrated and compact when the amount of $Ni_2O_3$ was 4.5 phr (Fig. 2c). The reason for the improvement of the flame-retardant properties with the addition of $Ni_2O_3$ is that Ni formed in the combustion process catalyzed the deposition of residual char and improved the density of char layers. When the amount of $Ni_2O_3$ was less than 7.5 phr, char layers began to collapse. It can be ascribed to uneven distribution of $Ni_2O_3$ particles when its content becomes too large. Otherwise, nickel particles, formed during combustion, also aggregate especially in the char layers, enhancing the strength of char layers and diminishing the flame retardancy efficiency.

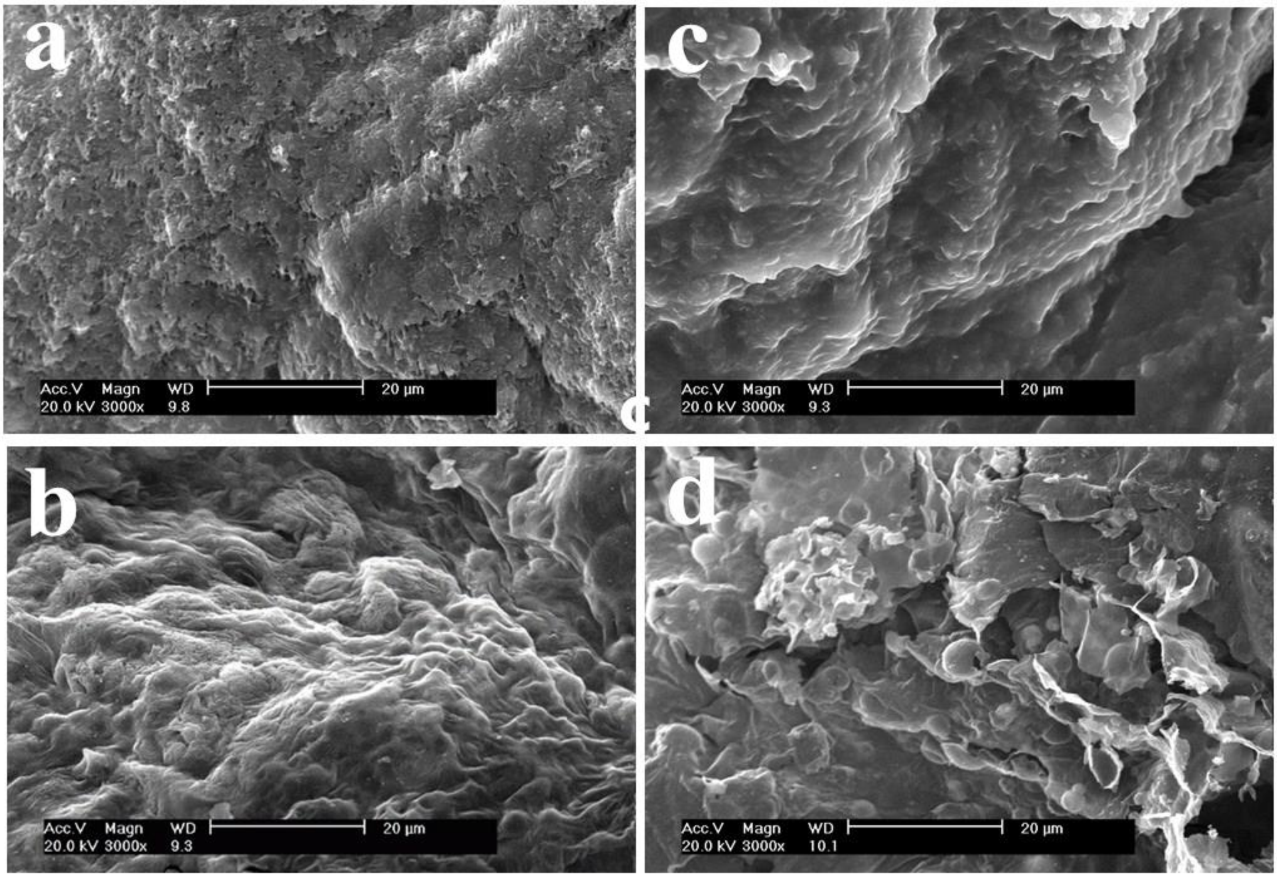

Fig. 2. SEM micrographs of char layers of flame-retardant TPU composites a-TPU/IFR; b- TPU/IFR/ $Ni_2O_3$-1.5; c-TPU/IFR/ $Ni_2O_3$-4.5; d-TPU/IFR/ $Ni_2O_3$-7.5.

### 3.4 Dispersion

Micrographs in Fig. 3 reveal the fracture surface morphologies of flame-retardant TPU/IFR composites. They show a smooth fracture surface without any obvious phase splitting phenomenon for the samples without $Ni_2O_3$ (Fig. 3a). A few local IFR agglomerations can be observed but still the additives were homogeneously distributed because of compatibility between IFR particles and TPU matrix. There was no evident reunion phenomenon when the amount of $Ni_2O_3$ reached to 1.5 phr (Fig. 3b). There should be no influence on the mechanical properties because this fracture surface was not much different from that of the original IFR system. Phase splitting phenomenon was still not obvious when $Ni_2O_3$ amount was 4.5 phr but fracture surface was rougher and a small amount of hollow structure pulled out (Fig. 3c). This observation showed that $Ni_2O_3$ within the system is not well compatible with the matrix. An obvious reunion phenomenon appeared when $Ni_2O_3$ was increased to an excess amount (7.5 phr) with most of the reunion particles diameters in the range of 5~10 μm. Larger particles with diameters of approximately 25 μm were also observed.

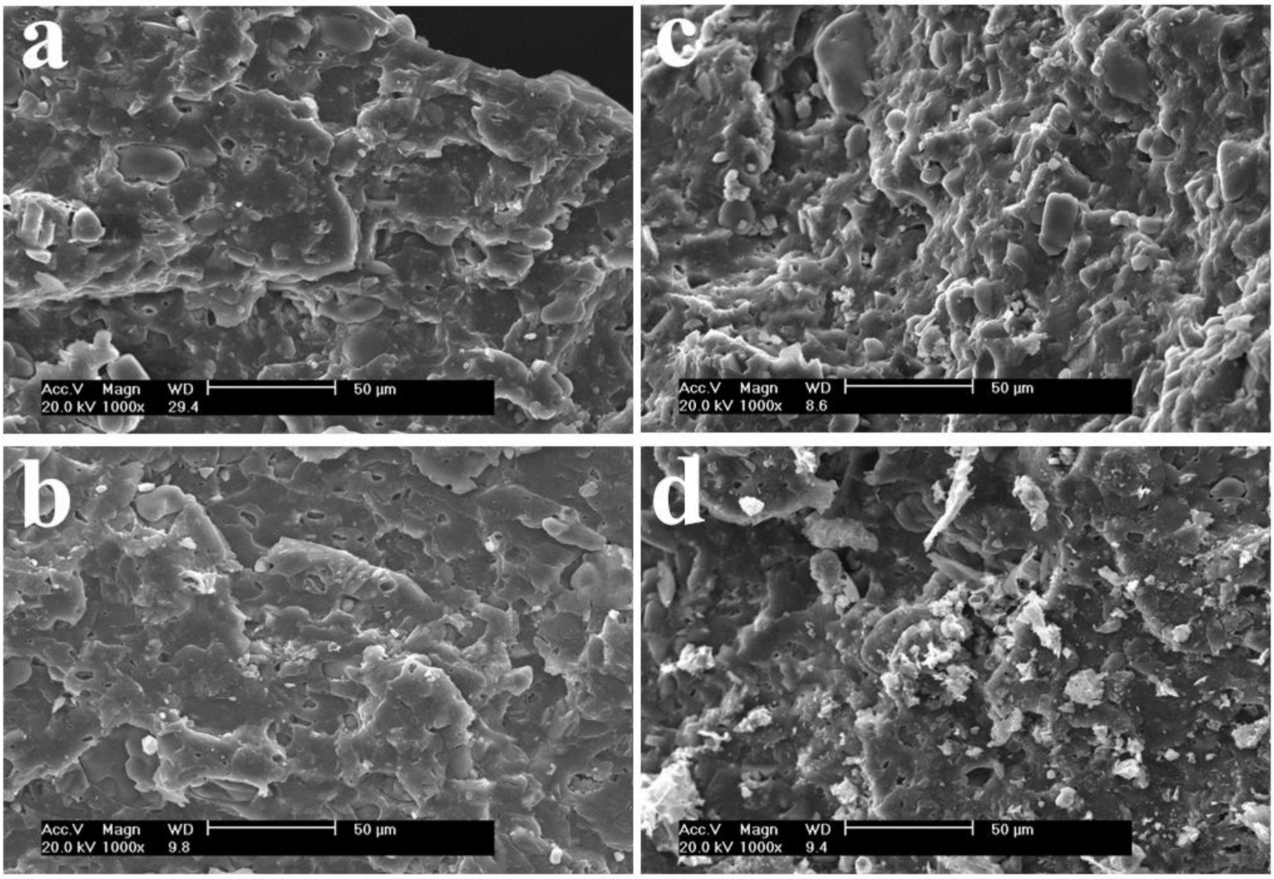

Fig. 3. SEM micrographs of fractured surface of flame-retardant composites a-TPU/IFR; b-TPU/IFR/ $Ni_2O_3$-1.5; c-TPU/IFR/ $Ni_2O_3$-4.5; d-TPU/IFR/ $Ni_2O_3$-7.5.

### 3.5 Mechanical properties and melt characteristics

In the examination of tensile properties of the flame retardant TPU (Fig. 4), with increase of $Ni_2O_3$ amount, the TPU/IFR-$Ni_2O_3$ system presented the downward trend of the tensile strength and elongation at break. The system revealed only a small increase in tensile strength and elongation at break when the amount of $Ni_2O_3$ was 1.5 phr. For this composition, tensile strength increased from 9.3 MPa (without $Ni_2O_3$) to 9.4 MPa (an increase of 1.1%), and the elongation at break increased from 595% (without $Ni_2O_3$) to 620% (an increase of 4.2%). This may be on the premise of uniform distribution of small amount of $Ni_2O_3$ particles in the matrix and the microporous structure. Microporous structure can be used as a stress concentrative point initiating crazes and terminating the extension of crack at the same time when the external force applies, thus, producing a small toughening effect on matrix. When the amount of $Ni_2O_3$ was greater than 1.5 phr, the tensile strength of TPU/IFR-$Ni_2O_3$ system tend to continuously decrease. As the amount of $Ni_2O_3$ reached 7.5 phr, the tensile strength decreased 29.0% from 9.3 MPa (without $Ni_2O_3$) to 6.6 MPa and elongation at break decreased 26.0% from 595% (without $Ni_2O_3$) to 440%. With consideration of the fracture surface analysis in micrographs of Fig. 3, the decline of mechanical properties can be ascribed to the compatibility between $Ni_2O_3$ and matrix. Because of the phase separation and agglomeration of $Ni_2O_3$ particles in matrix, there was a certain decline in tensile strength and elongation.

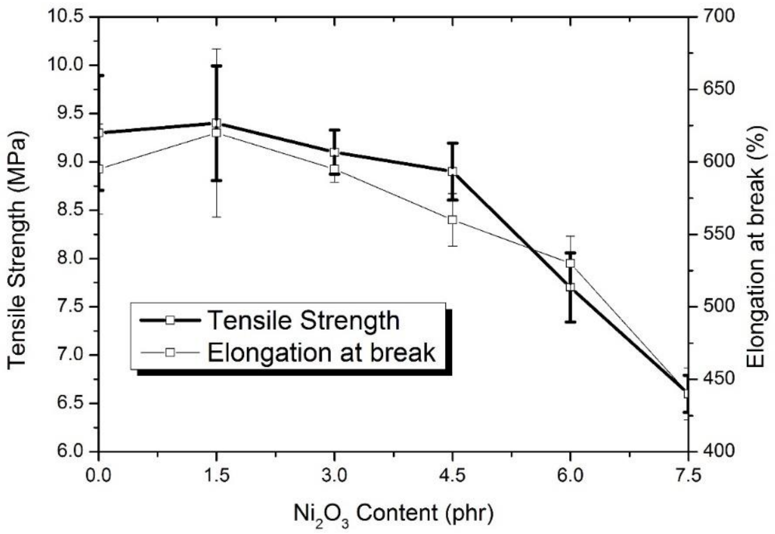

Fig. 4. Mechanical properties of flame-retardant TPU/IFR-Ni2O3 composites

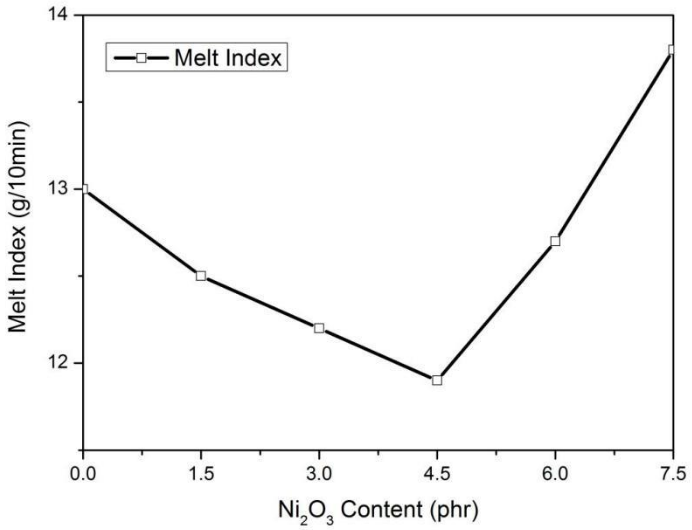

Fig. 5. Variations of MI values of flame-retardant TPU/IFR-$Ni_2O_3$ composites at different amounts of $Ni_2O_3$

The effect of $Ni_2O_3$ content on the melt index (MI) of flame-retardant TPU is shown in Fig. 5. The MI of TPU/IFR-$Ni_2O_3$ flame-retardant system declined after initial rising with the increase of $Ni_2O_3$ content. When the amount of $Ni_2O_3$ reached 4.5 phr, MI of the system decreased 8.5% from 13.0 g/10min (without $Ni_2O_3$) to 11.9 g/10min. This observation could be ascribed to $Ni_2O_3$ small particles at nanometer level that accelerate the TPU chain segment to form a "network-like" chaos when its mass fraction reaches a certain critical value that reduces the mobility of the melt[10]. When the amount of $Ni_2O_3$ reached 7.5 phr, the MI value increased 6.2% from 13.0 g/10min (without $Ni_2O_3$) to 13.8 g/10min. The rapid increase in melt mobility of this system must be due to the disappearance of $Ni_2O_3$ nano-effect and lubrication of chain segments when the $Ni_2O_3$ fraction in the composite increased.

## 4. Conclusions

There is an obvious synergistic effect between $Ni_2O_3$ and TPU/IFR flame-retardant system. $Ni_2O_3$ can evidently increase the density of residual char after combustion and enhance the flame-retardancy of TPU. The LOI value of composites increased from 30.0% to 34.2% and flame-retardant rating reached to UL 94 V-0 rating (4.2 mm) when 4.5 phr $Ni_2O_3$ was added. Moreover, addition of a small amount of $Ni_2O_3$ toughened the matrix. Tensile strength and elongation at break of the system slightly improved by addition of 1.5 phr $Ni_2O_3$. But, with the increase of the $Ni_2O_3$ amount, both tensile strength and elongation at break declined because of the poor compatibility with matrix. Effects of $Ni_2O_3$ in TPU were observed to be different from the catalytic charring phenomenon in nonpolar polyolefins, but improved the thermal degradation process of alkyl phosphate to form a denser char layer that plays an important role in heat resistance performance through blocking and improving the flame retardancy.

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