Effects of MXene on Nonisothermal Crystallization Kinetics of Isotactic Polypropylene

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ABSTRACT: MXenes, a family of two-dimensional transition-metal carbides/nitrides, have attracted great attention and shown promising application in polymer composites. In this study, a typical MXene Ti$_3$C$_2$T$_x$ was prepared by selective etching. The structure and morphology of Ti$_3$C$_2$T$_x$ were studied by X-ray diffraction (XRD), scanning electron microscopy, and transmission electron microscopy, and the results proved that Ti$_3$C$_2$T$_x$ was successively fabricated. Then, Ti$_3$C$_2$T$_x$/isotactic polypropylene composites with different Ti$_3$C$_2$T$_x$ dosages were fabricated, and the nonisothermal crystallization kinetics and melting behavior of the composites were investigated. The results indicated that when a small amount of Ti$_3$C$_2$T$_x$ was added, the crystallization parameters including the crystallization peak temperature and the crystallization rate increased, suggesting that crystallization was promoted. When the weight percentage of Ti$_3$C$_2$T$_x$ exceeded 1%, the crystallization parameters showed a reverse trend, suggesting that crystallization was hindered. The activation energy of composites with 0, 0.25, 0.5, and 1 wt % Ti$_3$C$_2$T$_x$ were calculated to be −164.5, −196.5, −193.8, and −147.95 kJ/mol, respectively, revealing that the crystallization of composites is concentration-dependent. The impact of Ti$_3$C$_2$T$_x$ dosage on the crystalline structure of the composites was studied using XRD. The related mechanism was proposed.

1. INTRODUCTION

In the past decade, two-dimensional (2D) materials have attracted significant attention and have been widely researched since single-layer graphene was exfoliated from graphite by the team of Novoselov and Geim in 2004.1 Due to their unique structure, 2D materials often possess superior physical, electronic, optical, and mechanical properties, leading to great potential application in many fields including energy storage, supercapacitor, composites, etc. Apart from graphene, many types of 2D materials such as metal–organic frameworks (MOFs),2,3 covalent–organic frameworks (COFs),4,5 and black phosphorus (BP)6 have been studied.6 In 2011, Gogotsi, Barsoum, and their team discovered and synthesized 2D transitional-metal carbides for the first time, which are called MXene.7 MXenes are a family of transition-metal carbides/nitrides with a general chemical formula M$_n$X$_n$T$_x$ (n = 1, 2, 3), where M stands for an early transition metal, X stands for C/N, and T$_x$ stands for possible surface terminations such as F \(^-\), O \(^-\), Cl \(^-\), and OH \(^-\). They are derived from MAX phases (A is usually elements from groups 12−16, such as Cd, Al, Si, P, S, Ga, Ge, As, Sn, Ti, Pb, and S\(^8\)), which have a layered hexagonal structure with two formula units per unit cell.8 Because A layer is relatively weakly bonded, the A layer atoms can be removed by selective etching. Since 2011, researchers have widely studied and synthesized about 30 different MXenes to explore their properties.9 Among the MXenes materials, titanium carbide (Ti$_3$C$_2$) is one of the most promising and widely studied10 and is usually synthesized by etching from its MAX phase Ti$_3$AlC$_2$. Like other 2D materials, MXenes have excellent properties due to their interesting structure and high surface area and therefore exhibit promising application in the fields of polymers. Many studies have been conducted to synthesize MXene-polymer composites. Zheng et al. produced Ti$_3$C$_2$/ultrahigh-molecular-weight polyethylene (UHMWPE) composites via the hot-pressing method.11 The results indicate that Ti$_3$C$_2$/UHMWPE composites exhibit improved mechanical properties and decreased antifriction performance. Woo et al. fabricated functionalized MXene (f-MXene)/boric acid (BA)/poly(vinyl alcohol) (PVA) composites, which show enhanced thermal stability and mechanical and oxygen gas barrier properties, making MXene/BA/PVA composite a potential gas barrier film.12 Liu et al. fabricated Ti$_3$C$_2$T$_x$rGO/thermoplastic polyurethane elastomer (TPU) composites via the solvent-mixing melt blending method, and the results indicated that the peak smoke production rate and the total smoke release
were remarkably decreased by 81.2 and 54.9%, respectively, with the addition of 2 wt % Ti3C2T6-rGO.13 Shi et al. prepared multifunctional nanohybrid Ti3C2T6 with melamine cyanurate (MCA) to fabricate Ti3C2T6@MCA/TPU nanocomposites and found that the nanocomposites show improved mechanical properties including high tensile strength of 61.5 MPa, high strain at failure of 58.84%, and remarkably high toughness of 175.4 MJ m−3.14

Isotactic polypropylene (PP), one of the most commonly used conventional thermoplastic materials, has been widely used in fields such as automobile, packaging, and electronic devices due to its low manufacturing cost, ease of processing, and other excellent properties such as high toughness, elasticity, transparency, and impermeability.15–17 However, mechanical properties such as weak impact strength and undesired thermal properties limit the application of polypropylene in some high-technology fields. Over the past few decades, incorporating inorganic fillers into a polymer matrix has become a widespread method to improve its physical properties.18 It has been found that nanoparticles such as graphene oxide (GO),19 surface-modified carbon black (CB),20 silicon dioxide (SiO2),21 etc., can improve the mechanical properties of polypropylene while promoting crystallization by functioning as nucleating agents. Since Ti3C2T6 has a similar structure to graphene oxide, it can be considered as a potential nanofiller to PP. Inspired by the nanoinfened structure, Shi et al. fabricated a Ti3C2T6/PP nanocomposite with improved mechanical and thermal properties by the melt blending methods. It was discovered that the strength, ductility, and modulus were simultaneously enhanced by adding 2 wt % Ti3C2T6.22

While current studies on the Ti3C2T6/PP nanocomposite mainly focus on the change in thermal and mechanical properties, the crystallization process is not investigated in depth. It is known that the crystallization behavior of crystalline polymers can affect the physical and mechanical properties, therefore understanding the crystallization kinetics is of great importance. In this work, Ti3C2T6/PP composites with different weight fractions were fabricated, followed by the analysis of the nonisothermal crystallization kinetics and melting behavior.

2. RESULTS AND DISCUSSION

2.1. Structure and Morphology of Ti3C2T6. To check the structure and morphology of the Ti3C2T6 powder, XRD, SEM, and TEM were conducted. As shown in Figure 1, the peaks of precursor Ti3AlC2 diminish gradually after etching. It is worth noting that the strongest (104) peak of Ti3AlC2 at 2θ ≈ 38.9° disappears, indicating the removal of the Al layer and thus the transformation from Ti3AlC2 to Ti3C2T6.23 It is worth noting that the (002) peak at around 9.6° shifts to 6.4° after etching, which is caused by the increase in the interlayer distance. Moreover, the broadening of the (002) peak after etching may be attributed to the decrease in the structural order.24

The morphology and chemical composition can be investigated by SEM and EDS. Figure 2a indicates that Ti3AlC2 powders exhibit a compact layered morphology that is often observed in ternary carbide.25 Figure 2b exhibits an accordion-like multilayer structure of Ti3C2T6 after etching, which is caused by exfoliation of the Al layer and suggests the success of the etching process.26 Moreover, it is observed that the layer structure expanded compared with the structure of original Ti3AlC2 which is possibly caused by the gas escaping during (i.e., H2) due to the exothermic nature of the reaction between HF and Al.27 From the EDS results, the Ti3C2T6 sample consists of Ti, C, O, F, and Al elements in the atomic ratio 21.9:28.3:27.7:20.5:1.6. During the etching process, two solid products may exist in the solution according to the equation

\[
\text{Ti3AlC2(s)} + 3\text{HF(l)} \rightarrow \text{Ti3C2T6(s)} + \text{AlF3(s)} + (3/2)\text{H2(g)}
\]  

The presence of the Al element suggests the existence of AlF3 impurities,28 which form small balls attached to the surface of Ti3C2T6.

Figure 3 shows that the diluted Ti3C2T6 dispersion has a light green color and shows the Tyndall scattering effect. From the TEM image (Figure 4), it can be observed that Ti3C2T6 has a sheet-like morphology, which is ultrathin and has a lateral size of a few hundred nanometers. Together with XRD, SEM, and EDS results, it can be concluded that Ti3C2T6 was successively synthesized by etching.

2.2. Nonisothermal Crystallization Kinetics of the Composites. In the following section, the investigation of the crystallization kinetics is performed on the PP/Ti3C2T6 composites. Figure 5 displays the cooling curve of each sample under cooling rates of 2, 10, 20, 30, and 40 °C/min. It can be seen that the cooling curves of the four samples have a similar variation tendency: as the cooling rate increases, the crystallization peak shifts toward lower temperature and becomes broader. Furthermore, the crystallization peak width (i.e., the difference between the onset and endpoint temperatures of crystallization, Tc−Tend) as well as the crystallization peak temperature Tc was calculated as indicators of the impact of Ti3C2T6 on the crystallization of the composites. Figure 6 shows Tc and Tc−Tend as a function of the cooling rate of four samples. For all samples, Tc and Tc−Tend both increase with a higher cooling rate. At higher cooling rates, PP chains have limited time to move and rearrange in order; therefore, the crystallization process requires a larger extent of supercooling.

The addition of Ti3C2T6 altered the crystallization behavior; when the weight percentage of Ti3C2T6 increases from 0 to 0.25 and 0.5%, the values of both crystallization peak temperature and crystallization peak width increase. When
the weight percentage of Ti$_3$C$_2$T$_x$ further increases to 1%, the crystallization peak temperature drops to a value lower than of neat PP. The crystallization peak width first declines with the addition of more Ti$_3$C$_2$T$_x$ then starts to grow when the weight fraction of Ti$_3$C$_2$T$_x$ is 1 wt %. At a higher cooling rate (30 and 40 °C/min), the crystallization peak width of 1 wt % Ti$_3$C$_2$T$_x$ is the highest. A possible explanation has been proposed here. To the best of our knowledge, the crystallization theory divides crystallization into two processes: nucleation and growth. For neat PP, the crystallization nucleation is homogeneous. When Ti$_3$C$_2$T$_x$ are added to the PP matrix, they might tend to be adsorbed on the polymer chains due to their highly active surface and therefore act as heterogeneous nucleation sites.\textsuperscript{11,28} In other words, the introduction of Ti$_3$C$_2$T$_x$ might provide more nucleation sites and then promote the crystallization process. The more the nucleation sites, the better the ability of the polymer to crystallize. As a result, the crystallization parameters including the crystallization peak temperature shift to higher values. In addition, polypropylene contains chains with different crystallization abilities. When the crystallization process is promoted, more PP chains can participate in crystallization. On the one hand, the part of chains with stronger crystallization ability becomes more easily crystallize, so $T_{\text{onset}}$ shifts to a higher temperature. On the other hand, the part of chains that cannot crystallize before can now crystallize but requires a larger extent of overcooling; therefore, $T_{\text{endpoint}}$ may shift to a lower temperature. As a result, the crystallization peak width may become wider.

The cumulative relative crystallinity vs crystallization time curve is shown in Figure 7. It is obvious to see that the addition of Ti$_3$C$_2$T$_x$ leads to a decrease in the crystallization time. To further analyze the crystallization behavior, half-crystallization time $t_{1/2}$ (i.e., the time when relative crystallinity reaches 50%) can be calculated. Table 1 reveals that at a lower cooling rate, the value of $t_{1/2}$ decreases continuously with the addition Ti$_3$C$_2$T$_x$ but increases again when the weight fraction of Ti$_3$C$_2$T$_x$ reaches 1%. At a higher cooling rate, $t_{1/2}$ of PP + 0.25% Ti$_3$C$_2$T$_x$ is smaller than those of others. It can be concluded that the crystallization rate tends to first increase and then decrease as more Ti$_3$C$_2$T$_x$ is added to the polymer matrix.
The Avrami equation is often used to describe the isothermal crystallization kinetics by eq 2

\[ X(t) = 1 - \exp(-kt^n) \]  

where \( X(t) \) is the relative crystallinity, \( t \) is the crystallization time, \( k \) is the crystallization rate constant, and \( n \) is the named Avrami exponent of which the value varies between 1 and 4 depending on the mechanism of nucleation and growth.\(^{29}\) This equation can be expressed in the following form

\[ \ln[-(1 - X)] = n \ln t + \ln k \]  

Since the Avrami equation describes the crystallization process under constant temperature, the Jeziorny model\(^{30}\) was applied to account for the nonisothermal crystallization condition.\(^{31,32}\) In the Jeziorny model, the parameter \( k \) is modified by introducing the cooling rate \( \dot{\theta} \), as in the following equation

\[ \ln k_c = (\ln k) / \dot{\theta} \]  

The crystallization activation energy \( E_c \) is calculated from the plot of the crystallization peak temperature \( T_c \) and cooling rate \( D \) through the Kissinger method,\(^{33-35}\) as shown in eq 5.
where $R$ is the universal gas constant, $D$ is the cooling rate, and $E_c$ is the activation energy. By integration, the equation can be expressed as

$$
\ln \left( \frac{D}{T_c^2} \right) = -\frac{E_c}{R}
$$

(5)

From eq 6, the graph of $\ln(D/T_c^2)$ vs $(1/T_c)$ can be plotted and thereby the slope ($-E_c/R$) and activation energy can be calculated. The Kissinger plot of the four samples is shown in Figure 8; the activation energy of the four samples follows the order: PP + 0.5% Ti$_3$C$_2$T$_x$ > PP + 0.25% Ti$_3$C$_2$T$_x$ > PP + 1% Ti$_3$C$_2$T$_x$ > PP.

Table 2 indicates that the value of $\ln(k_c)$ first increases then decreases with a continuous increase in the fraction of

**Figure 7.** Plots of relative crystallinity as a function of time of (a) neat PP, (b) PP + 0.25% Ti$_3$C$_2$T$_x$, (c) PP + 0.5% Ti$_3$C$_2$T$_x$, and (d) PP + 1% Ti$_3$C$_2$T$_x$ at different cooling rates.

**Figure 8.** Plots of $\ln(D/T_c^2)$ versus $1/T_c$ of the four samples to calculate the activation energy $E_c$ by the Kissinger method.
Ti$_3$C$_2$Tx. Since the value of ln($k_c$) is related to the bulk crystallization rate, the results suggest that the crystallization rate would start to decrease once Ti$_3$C$_2$Tx is added over a certain limit. It is known that the larger the activation energy, the more difficult the motion of polymer chains and thus greater the energy required to release during the crystallization process. The activation energies of PP, PP + 0.25% Ti$_3$C$_2$Tx, PP + 0.5% Ti$_3$C$_2$Tx, and PP + 1% Ti$_3$C$_2$Tx are $-164.5$, $-196.5$, $-193.8$, and $-148.0$ kJ/mol, respectively. The variation tendency of the activation energy is the same as that of the crystallization rate and the crystallization temperature. The crystallization parameters including the crystallization peak temperature, half-crystallization time, and nonisothermal crystallization kinetic constant suggest that with the addition of Ti$_3$C$_2$Tx, the crystallization process is accelerated during which Ti$_3$C$_2$Tx might act as heterogeneous nuclei while the energy barrier is lowered. With the further addition of Ti$_3$C$_2$Tx, a rigid framework might be formed and impose a strong restrain on the crystal growth. Therefore, at higher concentrations of Ti$_3$C$_2$Tx, the crystallization process would be surpassed, the crystallization parameters including the crystallization peak temperature and crystallization rate tend to shift to lower values.

Table 2. Crystallization Kinetics Parameters of Four Samples

| Sample         | $E_c$ (kJ/mol) | Cooling Rate (°C/min) | $N$  | $\ln(k_c)$ | $\ln(k)$ |
|----------------|----------------|-----------------------|-----|-------------|-----------|
| Neat PP        | $-164.5$       | 5                     | 2.6 | $-0.24$     | $-0.05$   |
|                |                | 10                    | 2.8 | 0.67        | 0.07      |
|                |                | 20                    | 2.9 | 1.67        | 0.08      |
| PP + 0.25% Ti$_3$C$_2$Tx | $-196.5$       | 5                     | 2.6 | 0.03        | 0.01      |
|                |                | 10                    | 2.9 | 0.83        | 0.08      |
| PP + 0.5% Ti$_3$C$_2$Tx | $-193.8$       | 5                     | 2.6 | 0.11        | 0.02      |
|                |                | 10                    | 2.9 | 0.90        | 0.09      |
| PP + 1% Ti$_3$C$_2$Tx | $-148.0$       | 5                     | 2.6 | $-0.03$     | $-0.01$   |
|                |                | 10                    | 3.0 | 0.61        | 0.06      |
|                |                | 20                    | 3.2 | 1.63        | 0.08      |
|                |                | 40                    | 3.2 | 2.20        | 0.07      |

Figure 9. Melting curves of (a) neat PP, (b) PP + 0.25% Ti$_3$C$_2$Tx, (c) PP + 0.5% Ti$_3$C$_2$Tx, and (d) PP + 1% Ti$_3$C$_2$Tx after the previous cooling cycle. The rate labeled above each curve is the cooling rate of the previous cooling cycle.
where $\Delta H_m$ is the enthalpy of melting, $\Delta H_0$ is the enthalpy of melting when the material is 100% crystalline, which is 209 J g$^{-1}$ for iPP in this case, and $x$ is the weight fraction of Ti3C2Tx in the sample.\(^{39}\) It can be seen from Figure 9 that the change in melting peak temperature $T_m$ is less obvious compared with crystallization peak temperature $T_c$. When the weight fraction of Ti3C2Tx increases, the melting peak width first declines and then increases. Figure 10 and Table 3 indicate that both the melting peak width and the relative degree of crystallinity of the samples follow the order: PP + 0.5% Ti3C2Tx > PP + 0.25% Ti3C2Tx > PP > PP + 1% Ti3C2Tx. Similar to crystallization rate and activation energy, the crystallinity of Ti3C2Tx/PP composite starts to decline when the weight fraction of Ti3C2Tx is 1%. This may arise from the aggregation of Ti3C2Tx, which restricts the chain movement and hinders the packing of polymer chains.

### 2.4. Wide-Angle X-ray Diffraction (WAXD) Characterization

PP is a semicrystalline polymer consisting of crystalline and amorphous phases. It is well-known that polypropylene has four crystalline forms $\alpha$, $\beta$, $\gamma$, and mesomorphic depending on the arrangement and packing of chains.\(^{40\text{-}42}\) Among them, the $\alpha$ form is most stable and commonly found in polypropylene; $\beta$ form is metastable but has a higher toughness. To investigate the crystallite form in Ti3C2Tx/PP composites, WAXD was conducted since each form has a unique diffraction pattern.

Apart from the diffraction angle $2\theta$ and lattice spacing, the crystallite dimension can also be calculated from the WAXD data by Debye–Scherrer’s equation

$$L = \frac{kl}{\beta \cos(\theta)}$$

where $k$ is the shape factor and the value is taken as 0.9, $L$ is the crystallite dimension, $\beta$ is the diffraction line width at half maximum (FWHM) intensity in radians, and $\theta$ is the diffraction angle at the maximum peak.

The WAXD patterns and data are displayed in Figure 11 and Table 4. There are mainly five peaks at around 13.9, 16.9, 18.6, 21.1, and 21.8°, which correspond to $\alpha$(110), $\alpha$(040), $\alpha$(130), $\alpha$(111), and $\alpha$(041), respectively. The distribution of the peaks proves that only $\alpha$-form exists in the composites. Therefore, the addition of Ti3C2Tx leads to the formation of the $\alpha$-crystal phase, and the same result was also observed in the work of Shi et al.\(^{22}\) It was found that the crystallinities of PP, PP + 0.25% Ti3C2Tx, PP + 0.5% Ti3C2Tx, and PP + 1% Ti3C2Tx are 50.40, 52.80, 54.70, and 49.72% respectively, obtained from the WAXD results. The variation tendency of the crystallinity calculated from DSC and WAXD is consistent. From Table 4 it can be known that the addition of Ti3C2Tx leads to a decrease in crystallite size. The sample that contains 0.5 wt % Ti3C2Tx has the smallest crystallite size.

### 3. CONCLUSIONS

In this work, Ti3C2Tx, a typical member of 2D MXenes was successfully fabricated by etching. Then, different weight fractions of Ti3C2Tx were mixed with PP by melt blending to study the nonisothermal crystallization kinetics of the resulting

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**Table 3. Melting Parameters Four Samples**

| cooling rate (°C/min) | parameter (°C) | neat PP | PP + 0.25% Ti3C2Tx | PP + 0.5% Ti3C2Tx | PP + 1% Ti3C2Tx |
|----------------------|----------------|---------|-------------------|-------------------|-----------------|
| 5                    | $T_m$          | 162.7   | 162.8             | 162.4             | 162.5           |
|                      | $X_c$ (%)      | 44.5    | 47.5              | 48.9              | 46.0            |
| 10                   | $T_m$          | 163.1   | 163.4             | 162.1             | 163.1           |
|                      | $X_c$ (%)      | 43.9    | 45.9              | 47.3              | 45.3            |
| 20                   | $T_m$          | 163.8   | 163.8             | 162.8             | 164.2           |
|                      | $X_c$ (%)      | 43.3    | 44.9              | 45.9              | 43.5            |
| 30                   | $T_m$          | 164.3   | 164.1             | 163.0             | 164.8           |
|                      | $X_c$ (%)      | 42.6    | 44.5              | 45.2              | 43.1            |
| 40                   | $T_m$          | 164.7   | 164.3             | 163.8             | 165.5           |
|                      | $X_c$ (%)      | 42.0    | 44.0              | 45.1              | 41.8            |
composites. When the amount of Ti₃C₂Tex added is increased from 0 to 0.5 wt %, the crystallization peak temperature and crystallization rate both increase, indicating that the crystallization process is promoted. Once the weight percentage of Ti₃C₂Tex reaches 1 wt %, the crystallization process requires larger supercooling, and the crystallization rate drops. The calculated activation energy is −164.5, −196.5, −193.8, and −147.95 kJ/mol, showing the same variation tendency as that of the crystallization peak temperature and rate. The WAXD results reveal that the crystallite size of nanocomposite with 0.5 wt % Ti₃C₂Tex is the smallest. Moreover, only α-form crystallite exists in the composites; therefore, it can be concluded that Ti₃C₂Tex acts as an α-form nucleating agent in the crystallization process.

4. EXPERIMENTAL

4.1. Materials. The Ti₃AlC₂ powders with 99% purity (400 mesh) were purchased from 11 Technology Co. Ltd., China. Lithium fluoride (LiF, 99% purity) was purchased from Aladdin Bio-Chem Technology Co. Ltd., China. Concentrated hydrochloric acid (HCl, 37 wt %) was purchased from Chengdu Kelong Chemical Reagent Factory, China. The isotactic polypropylene resin (trade name T38F) was obtained from Lanzhou PetroChemical Corp., China. The weighted-average molecular weight $M_w$ is 347 200 g/mol and average isotacticy tested by high-temperature solution $^{13}$C NMR is 97%.

4.2. Sample Preparation. 4.2.1. Etching of Ti₃AlC₂. In this work, the MAX phase Ti₃AlC₂ was etched by in situ HF formation. First, 19.5 mL of concentrated HCl was added to 20 mL of distilled water. LiF powders (2.5 g) were added to the diluted HCl under magnetic stirring. Then, 2.5 g of Ti₃AlC₂ powders was slowly added to the solution within 10 min to avoid overheating caused by the exothermic reaction. The mixture was held at 40 °C for 24 h under continuous stirring. When the etching was completed, the resulting mixture was purified by washing with distilled water and centrifuging at 8000 rpm for 10 min. This washing–centrifugation cycle was repeated until the supernatant reached a pH value of around 6.

Then, the sediment was added with distilled water, followed by ultrasonication in an ice-bath for 2 h and centrifugation. Finally, the supernatant was collected and dried under a vacuum.

4.2.2. Preparation of Ti₃C₂Tex/iPP Composites. In the first step, the Ti₃C₂Tex powder was mixed with PP granules to obtain the Ti₃C₂Tex/iPP masterbatch with a Ti₃C₂Tex concentration of 2.5 wt %. During the melt mixing process, a Brabender internal mixer with a 50 cm³ mixing chamber was used. The polypropylene granules and Ti₃C₂Tex were first slowly added to the internal mixer under a temperature of 190 °C and a rotation speed of 10 rpm and kept for 10 min. After that, the rotation speed was set to 50 rpm for 7 min. Then, the Ti₃C₂Tex/iPP masterbatch, Ti₃C₂Tex powder, and PP granules were mixed again in the internal mixer under the same conditions to prepare samples with different Ti₃C₂Tex weight percentages (0, 0.25, 0.5, and 1 wt %). After that, the mixture was compressed by a pressure molding machine at 8 MPa and 190 °C for further characterization.

4.3. Characterization. 4.3.1. Differential Scanning Calorimetry (DSC). All nonisothermal crystallization experiments were performed with Mettler Toledo DSC3 (Mettler, Switzerland) differential scanning calorimetry under a continuous nitrogen flow of 50 mL/min. The standard procedure for each experiment was as follows: 4–5 mg of the sample was weighed, heated to 200 °C at a rate of 10 °C/min, and held for 5 min to eliminate previous thermal history. Then, the sample was cooled to 50 °C at different cooling rates, i.e., 5, 10, 20, 30, and 40 °C/min, to analyze the crystallization behavior. After cooling, the sample was heated.

| parameters | sample | (110) | (040) | (130) | (111) | (041) |
|------------|--------|-------|-------|-------|-------|-------|
| $2\theta$ (deg) | neat PP | 13.9  | 16.7  | 18.3  | 20.9  | 21.7  |
|              | $+$ 0.25% Ti₃C₂Tex | 14.1  | 16.9  | 18.5  | 21.2  | 21.8  |
|              | $+$ 0.5% Ti₃C₂Tex  | 14.2  | 17.0  | 18.6  | 21.1  | 21.9  |
|              | $+$ 1% Ti₃C₂Tex  | 14.2  | 17.0  | 18.6  | 21.1  | 21.9  |
| $d$-spacing (Å) | neat PP | 6.4   | 5.3   | 4.8   | 4.2   | 4.1   |
|              | $+$ 0.25% Ti₃C₂Tex | 6.3   | 5.2   | 4.8   | 4.2   | 4.1   |
|              | $+$ 0.5% Ti₃C₂Tex  | 6.2   | 5.2   | 4.8   | 4.2   | 4.0   |
|              | $+$ 1% Ti₃C₂Tex  | 6.2   | 5.2   | 4.8   | 4.2   | 4.1   |
| $L$ (nm) | neat PP | 13.1  | 14.8  | 12.1  | 12.6  | 8.4   |
|              | $+$ 0.25% Ti₃C₂Tex | 11.0  | 12.6  | 9.4   | 8.2   | 9.9   |
|              | $+$ 0.5% Ti₃C₂Tex  | 13.0  | 14.3  | 10.9  | 10.2  | 8.3   |
|              | $+$ 1% Ti₃C₂Tex  | 12.7  | 14.3  | 10.8  | 16.6  | 10.1  |
from 50 to 200 °C at a rate of 10 °C/min to analyze the melting behavior.

The relative crystallinity ($X_r$) of the sample at a given crystallization time ($t$) could be calculated using the following equation

$$X_r = \int_0^t \left( \frac{dH}{dt} \right) dt / \int_0^\infty \left( \frac{dH}{dt} \right) dt$$

(9)

The half time of crystallization ($t_{1/2}$) can be calculated from the curve when the relative crystallinity is 50% and can be used to evaluate the crystallization rate. At an identical cooling rate, a lower crystallization half time indicates a higher overall crystallization rate.

4.3.2. X-ray Diffraction (XRD). The XRD patterns of Ti$_3$AlC$_2$, Ti$_3$C$_2$T$_x$, and Ti$_3$C$_2$T$_x$/PP composites were obtained through a diffractometer (Ultima IV, Rigaku, Japan). The wavelength of Cu Kα radiation was $\lambda = 0.154$ nm and the scanning rate was $2^\circ$/min. For Ti$_3$AlC$_2$, and Ti$_3$C$_2$T$_x$ powder samples were used and spectra were recorded in the range of $2\theta = 2^\circ$–$80^\circ$. Wide-angle X-ray diffraction (WAXD) was applied for Ti$_3$C$_2$T$_x$/PP composites; the samples were first hot molded into 1 mm thick sheets before taking the measurements. The scanning range was $2\theta = 5^\circ$–$40^\circ$.

4.3.3. Scanning Electron Microscopy (SEM) and Energy-Dispersive Spectroscopy (EDS). The morphologies and composition of precursor Ti$_3$AlC$_2$ and Ti$_3$C$_2$T$_x$ particles were observed via scanning electron microscopy (SEM, Apreo S HiVoc, Thermo Fisher Scientific) equipped with energy-dispersive spectroscopy (EDS).

4.3.4. Transmission Electron Microscopy (TEM). To further analyze the structure of Ti$_3$C$_2$T$_x$, TEM (Tecnai G2 F20 S-TWIN, FEI) was performed under an accelerating voltage of 200 kV. The TEM sample was prepared by dispersion in distilled water and under ultrasonication for 30 min; then, the dispersion was dropped on the copper grid for further observation.

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**Notes**

The authors declare no competing financial interest.

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