Structure and Crystallization Behavior of Poly(ethylene oxide)/Ti₃C₂T_x MXene Nanocomposites

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Abstract

MXenes represent a new family of 2D transition metal carbides that has attracted a great deal of attention in various applications because of their unique electrical, thermal, and mechanical properties. In this work, we report on the structure and crystallization behavior of poly(ethylene oxide)(PEO)/MXene nanocomposites. MXene Ti₃C₂T_x (where T is a surface termination) was synthesized and used as the nanofiller to form polymer nanocomposites using a solution blending method. Their morphologies, structures and crystallization behaviors were investigated using transmission electron microscopy, atomic force microscopy, polarized light microscopy, wide angle X-ray diffraction and differential scanning calorimetry. Both non-

isothermal and isothermal crystallization behaviors have been studied. We show that the presence of 2D $\text{Ti}_3\text{C}_2\text{T}_x$ accelerates PEO crystallization at very low MXene contents, while it inhibits PEO crystallization as the loading increases. The fastest crystallization rate was observed at 0.5 wt% MXene content. This was attributed to the competition of nucleation and confinement effect of the 2D filler.

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INTRODUCTION

Nanoparticles have recently attracted tremendous attention because of their fascinating mechanical, electrical and optical properties.[1-3] Numerous types of polymers have been used to form polymer brushes on nanoparticle surfaces in order to stabilize the latter.[3, 4] On the other hand, a variety of nanoparticles have been blended with polymers (or block copolymers) to form nanocomposites.[5-7] Last twenty years have witnessed significant progresses in the field of polymer nanocomposites, and they have shown fascinating properties compared with neat

polymers.[8, 9] Semi-crystalline polymers are widely used in polymer nanocomposites. Nanosized fillers such as one-dimensional (1D) carbon nanotubes (CNTs)[10-23] and two dimensional (2D) nanoclays,[17, 24-28] and graphene nanosheets (GNS) are known to affect the crystallization of polymer matrices.[29-35] For example, crystallization of poly(L-lactide) (PLLA) can be accelerated by both CNT and GNS. Compared to neat PLLA, the half-crystallization time ($t_{1/2}$) is shortened for PLLA/CNT and PLLA/GNS nanocomposites. Interestingly, the induction time was shortened when the CNT content increased from 0.05 wt.% to 0.1 wt.%, while the inverse trend was found in PLLA/GNS composites.[29] For isotactic polypropylene (iPP)/GNS nanocomposites, compared to neat iPP, $t_{1/2}$ is reduced by more than 50% when adding 0.05 wt.% GNS in iPP matrices. It has also been found that the glass transition temperature increases upon adding reduced graphene oxide (RGO), which was attributed to the restriction of polymer chain motion due to hydrogen bonding between the PVA chains and the RGO.[31-33] Both Yang *et al.*[33] and Salavagione[32] reported that the crystallinity decreases from ~ 50 wt.% of neat PVA to near 0% at high graphene content. Liang *et al.*[31] reported no obvious change in crystallinity or melting temperatures. Recently, we reported epitaxial growth of polyethylene, PE, on RGO.[36]

MXenes are a new family of 2D transition metal carbides and/or nitrides, typically produced by selectively etching out the A layers (groups 13 and 14 elements mostly) from the MAX phases. The latter are layered hexagonal ternary carbides and nitrides, where M is an early transition metal, X is carbon and/or nitrogen. [37] Since the MXene surfaces are terminated by O, OH, and/or F groups, they are best described as $M_{n+1}X_nT_x$, where T is a terminating group (O, OH or F), and x is their number, n is the number of X (vary from 1, 2, to 3). MXenes have attracted a great deal of attention in various applications due to their unique electrical [37-45],

thermal[37, 40], and mechanical properties.[38, 42] However, to our knowledge, there are very few reports in the literature on polymer-MXene nanocomposites[42] or polymer-MAX phase nanocomposites.[40] A recent paper was published in which $\text{Ti}_3\text{C}_2\text{T}_x$ /polydiallyldimethylammonium chloride and $\text{Ti}_3\text{C}_2\text{T}_x$ /polyvinyl alcohol (PVA) composites were fabricated. The composites were flexible and quite conductive. The tensile strength of the $\text{Ti}_3\text{C}_2\text{T}_x$ /PVA composites were significantly enhanced compared to neat $\text{Ti}_3\text{C}_2\text{T}_x$ or PVA films.[42]

Herein, we report on the structure and crystallization behavior of poly(ethylene oxide) (PEO)/MXene nanocomposites. Ti_3AlC_2 was selected as the MAX precursor to synthesize $\text{Ti}_3\text{C}_2\text{T}_x$ MXene because its exfoliation and delamination are reasonably well understood.[37] This selective dissolution of the ‘A’ element has been realized by immersing fine powders of certain MAX phases in fluoride-containing aqueous etchants such as hydrofluoric acid or hydrochloric acid with dissolved lithium fluoride.[37] [39] $\text{Ti}_3\text{C}_2\text{T}_x$ /PEO nanocomposites were fabricated, and the polymer's crystallization behavior was systematically characterized. PEO was chosen as the polymer matrix because it is widely used in solid polymer electrolytes (SPEs), for its high dielectric constant and strong lithium ion solvating capability.[46-54] Both non-isothermal and isothermal crystallization behaviors were systematically studied. Compared with pure PEO, PEO-based nanocomposite SPEs have shown increased ionic conductivity effectively, electrochemical stability and mechanical strength.[49, 54-60] Our ultimate goal is to fabricate PEO/MXene nanocomposite SPEs for energy storage.

EXPERIMENTAL DETAILS

Materials

PEO (average $M_n \sim 300$ kDa) and N,N-dimethylformamide (DMF) were purchased from Sigma-Aldrich and used as-received. Commercially available Ti_2AlC powders were purchased from Kanthal in Sweden. The TiC and lithium fluoride (LiF , 98%) powders were purchased from Alfa Aesar. 6 M hydrochloric acid (HCl) was purchased from Fisher Scientific. Polypropylene Membranes – with a $0.22 \mu m$ pore size – were purchased from Celgard LLC.

Synthesis of Ti_3AlC_2

The synthetic procedure of Ti_3AlC_2 and $Ti_3C_2T_x$ was reported in previous publication.[39] In brief, Ti_2AlC and TiC powders were first mixed together in a 1:1 molar ratio (accounting for the ≈ 12 wt.% of Ti_3AlC_2 already existing in the Ti_2AlC powder) in a ball-mill for 18 h with yttria-stabilized zirconia milling balls. The mixture was then placed in an alumina, Al_2O_3 , crucible and heated in an Al_2O_3 tube furnace, at a rate of $5^\circ C/min$ to a temperature of $1350^\circ C$ under a constant flow of argon (Ar) gas. The mixture was held at $1350^\circ C$ for 2 h before the furnace was cooled to room temperature. The resulting lightly sintered brick was ground into powder with a milling bit and passed through a sieve (U.S Standard Sieve Mesh #400) to ensure particle sizes $< 38 \mu m$.

Synthesis of exfoliated $Ti_3C_2T_x$

First, 1.32 g of LiF was dissolved in 6 M HCl, and the solution was stirred until all the LiF was dissolved.[39] 2.0 g of the-400 mesh Ti_3AlC_2 powders were then immersed in 20 ml of the LiF/HCl solution. Because of the exothermic nature of the reaction, the Ti_3AlC_2 was added in small portions over a 5-minute period to avoid overheating the solution. The mixture was heated and stirred on a magnetic hot plate for 24 h at 40 °C. The resulting solution was washed with distilled water and centrifuged to separate the reaction product from the supernatant, which was decanted. This step was repeated until the supernatant had a pH of ~ 6 . The final product was diluted with water and filtered onto a 0.22 μm pore size membrane of polypropylene.[39]

Preparation of few-layer $\text{Ti}_3\text{C}_2\text{T}_x$ solution

The $\text{Ti}_3\text{C}_2\text{T}_x$ multilayer powders were dispersed in deionized water by tip ultrasonication in an ice bath for 2 h, while bubbling Ar gas through the mixture. The suspension was centrifuged at 2400 ref for 1 h. The supernatant was separated from the sediment powders to obtain a black colloidal suspension of mostly single/few $\text{Ti}_3\text{C}_2\text{T}_x$ layers. To determine its solid content, a known volume of the colloidal suspension was filtered onto a polypropylene membrane and weighed after drying. The solid loading was determined to be ≈ 0.19 mg/mL based on the weight change of the membrane.

Preparation of PEO/ $\text{Ti}_3\text{C}_2\text{T}_x$ polymer nanocomposites

PEO/ $\text{Ti}_3\text{C}_2\text{T}_x$ polymer nanocomposites were fabricated using a solution mixing/precipitation method. In brief, stock solutions of 0.02 wt.% of the $\text{Ti}_3\text{C}_2\text{T}_x$ in water and 1.25 wt% of PEO in water were first prepared. Pre-calculated amounts of stock solutions were then mixed while being sonicated, so that PEO/ $\text{Ti}_3\text{C}_2\text{T}_x$ nanocomposites with 0%, 0.1%, 0.5%,

1%, 2% and 5% MXene by weight were produced. The mixtures were further stirred for 2 h, and precipitated in cold ethanol. Precipitants were filtered out into films, and the solution after filtering was colorless. The nanocomposite films were dried in a vacuum oven for one week at 32°C before use.

Characterization Methods

JEOL JEM2100 transmission electron microscopy (TEM) with an accelerating voltage of 120 kV was used to measure the size distribution of the MXene suspension. The MXene suspension was spin coated onto a carbon-coated TEM grid, and dried under vacuum before TEM experiments. Tapping-mode atomic force microscopy (AFM) experiments were conducted on a Bruker Multimode 8 AFM (Bruker Nano, Santa Barbara, CA). Specifically, Bruker NCHV-A tips (aluminum coated silica, resonance frequency ~ 320 kHz, spring constant ~ 42 N/m, tip radius ~ 8 nm) were used for imaging. After sonication, the MXene suspension was spin coated onto a clean glass slide (cleaned by Piranha solution overnight and washed with isopropanol). The sample was dried under vacuum overnight.

Optical microscopy experiments were conducted using a polarized light microscope (PLM) (an Olympus BX-51) equipped with a Mettler Toledo hot stage (MTFP82HT). 2D wide-angle X-ray diffraction (WAXD) was performed using a Rigaku S-MAX 3000 SAXS system, with a Cu K α wavelength of 1.54 Å. WAXD patterns were collected using an image plate. Powder X-ray diffraction was performed on a Rigaku SmartLab diffractometer using Cu K α radiation using a step size of 0.02° and dwell time of 1 s per step. Thermogravimetric analysis (TGA) tests were conducted using a Perkin-Elmer TGA 7 under flowing nitrogen (N₂) in the 50

to 800 °C temperature range at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) experiments were conducted using DSC Q2000 with Tzero pans from TA Instruments for non-isothermal and isothermal experiments.

RESULTS AND DISCUSSION

Structure and Morphology of PEO/MXene nanocomposites

Figure 1a shows the schematics of a typical MXene structure, and **Figure 1b** depicts a TEM image of MXene nanoplatelets after ultrasonication. Small, irregular 2D platelets can be clearly seen. **Figure 1c** is an enlarged view of a MXene nanoplatelet and **Figure 1d** shows a histogram of the particle size distribution. Since the platelets are irregular in shape, their sizes were estimated using the square root of their areas. Based on the histogram, the average size of the platelets is ~ 88 nm, the median and mode lie around the range of 50 nm, and the size ranges from 45~388 nm. Most of the nanoplatelets are relatively isotropic in the sheet plane with a width/thickness aspect ratio of approximately ~ 10. The TEM image also suggests that most of the MXene platelets are thin, which was confirmed by measuring the thicknesses of select platelets in an AFM. **Figure 1e** shows an AFM image of a relatively large as-obtained MXene platelet, about 200 × 400 nm in size. The corresponding height profile shown in the inset of **Figure 1e** reveals that the average thickness of this platelet is ~ 5 nm, which corresponds to ~ 4-5 MXene layers (a $\text{Ti}_3\text{C}_2\text{T}_x$ monolayer is ~ 1 nm thick). A typical selective area electron diffraction, SAED, pattern of an individual platelet is shown in the inset of **Figure 1b**. The [001] zone hexagonal diffraction typical of the parent MAX phases is observed, indicating that the in-plane crystalline structure was not destroyed by the sonication process. Therefore, our sample preparation process provides an efficient means to fabricate few-layered MXene nanoplates, with an average size of ~ 88 nm and an intact crystalline structure of the basal planes.

Figure 1. 2D $\text{Ti}_3\text{C}_2\text{T}_x$ platelets. (a) Chemical structure of a typical MXene. (b, c) TEM image of the as prepared MXene. Inset shows a typical selected area electron diffraction pattern of a single platelet. (d) Histogram of particle sizes. (e) AFM image of a nano platelet. The inset height profile shows an average height of ~ 5 nm.

These MXene nanoplatelets were then solution blended with PEO to form polymer nanocomposites following the procedure described in the experimental section. A total of 5 composites, with different MXene contents were prepared, henceforth referred as MXEO- δ , where MX denotes the MXene used, EO represents the PEO matrix, and δ is a number index of each sample. TGA experiments were firstly used to study the thermal stability and the results are shown in **Figure 2a**. **Figure 2b** plots the weight changes (5% weight change temperature, $T^{5\%}$,

and peak degradation temperature, T^{peak}) as a function of temperature for the 5 composites fabricated, and the results are also depicted in **Table 1**. It appears that the thermal stability of the samples does not change significantly with the addition of 2D MXene.

Figure 2. Thermal stability of MXEO- δ nanocomposites. (a) TGA curves of PEO, MXene, and PEO/MXene nanocomposites. (b) Plot of $T^{5\%}$ and T^{Peak} vs. MXene content.

Table 1. Thermal characterization of PEO/MXene nanocomposites.*

Sample	MXene Content (wt.%)	$T^{5\%}$ (°C)	T^{peak} (°C)	Crystallinity heating (%)	Crystallinity Cooling (%)	T_{c-peak} (°C)	$T_{c-onset}$ (°C)	T_{m-peak} (°C)	$T_{m-onset}$ (°C)
PEO	0	334.2	385.3	59.2	58.6	44.4	46.8	64.0	61.1
MXEO-1	0.1	325.6	385.0	59.1	58.0	44.9	47.4	63.9	61.3
MXEO-2	0.5	342.5	392.3	59.6	59.5	45.8	47.9	64.0	61.5
MXEO-3	1	344.6	391.7	58.7	58.0	44.9	46.8	63.8	61.4
MXEO-4	2	340.9	382.8	59.4	58.2	42.9	45.7	63.0	60.5
MXEO-5	5	330.0	387.1	53.9	53.6	45.2	47.0	63.6	61.3

* $T^{5\%}$: 5% weight change temperature based on TGA; T^{peak} : peak degradation temperature based on TGA; T_{c-peak} : Peak crystallization temperature; $T_{c-onset}$: Onset crystallization temperature; T_{m-peak} : Peak melting temperature; $T_{m-onset}$: Onset melting temperature.

Figure 3 shows typical room temperature PLM images of PEO and MXEO- δ films.

These films were first melted at 100 °C and then quenched to 25 °C. The PEO spherulitic structure can be clearly seen in the neat PEO (**Figure 3a**) and MXEO-1 (**Figure 3b**), while the spherulite size decreases from $\approx 300 \mu\text{m}$ to about $7 \mu\text{m}$ with increasing MXene content (**Figure 3c-e**). This is apparently due to the increased nucleation sites of the composites as the filler content increases. Note that MXEO-5 PLM sample is opaque due to the high MXene contents, and we opted not to include this sample in the PLM.

Figure 3. PLM micrographs of neat PEO and different ratio of MXene with PEO. a) Pure PEO; b) MXEO-1; c) MXEO-2; d) MXEO-3; e) MXEO-4. The scale bars are 100 μm .

The crystal structure of the MXEO composites was studied using WAXD. Figure 4a shows the 2D WAXD pattern of MXEO samples. Multiple concentric diffraction rings can be clearly observed. The azimuthal integration profile of **Figure 4a** is shown in **Figure 4b**. In all the samples investigated, two major diffraction peaks at $2\theta = 19.15^\circ$ and 23.3° - corresponding to the (120) and (032) planes of the PEO monoclinic crystal structure, respectively - are observed. **Figure 4c** shows typical WAXD patterns of $\text{Ti}_3\text{C}_2\text{T}_x$ powder (red curve). (002) diffractions are clearly seen in the pattern, while the stars indicate diffractions from the precursor MAX phase. After dispersing the $\text{Ti}_3\text{C}_2\text{T}_x$ powder in water under sonication, and vacuum filtering the resultant suspension, $\text{Ti}_3\text{C}_2\text{T}_x$ films are obtained and the corresponding WAXD pattern is shown in **Figure 4c** (blue curve). Only (00 l) diffractions can be seen, with increased full width of half maximum, indicating the inter-layer ordering is decreased due to the sonication process. Interestingly, the strong (002) MXene diffraction peak is absent in the WAXD patterns of the

nanocomposites (**Figure 4b**), proving that the MXene particles have been exfoliated into few layers, and the long range layer correlation of the MXEO is disrupted.

Figure 4. WAXD patterns of (a, b) PEO/MXene nanocomposites. (b) shows the azimuthal integration of the diffraction patterns in (a). (c) XRD patterns of $\text{Ti}_3\text{C}_2\text{T}_x$ powders before sonication (red) and a free-standing $\text{Ti}_3\text{C}_2\text{T}_x$ film (blue). The latter was prepared by vacuum filtration of a colloidal $\text{Ti}_3\text{C}_2\text{T}_x$ suspension.

Crystallization behavior of the PEO/MXene nanocomposites

The crystallization behavior of the MXEO composites was investigated first using non-isothermal DSC experiments. **Figures 5a** and **b** depict, respectively, the first cooling and second heating thermograms of the nanocomposites. The first cooling thermograms show that the peak crystallization temperature, $T_{c\text{-peak}}$, slightly upshift ($\sim 1.4\text{ }^{\circ}\text{C}$) as the 2D nanofiller content increases up to 1%, at which point a downshift of $3\text{ }^{\circ}\text{C}$ was observed. MXEO-4 showed the lowest crystallization temperature. When the MXene content increased from 2% to 5%, $T_{c\text{-peak}}$ increases by $3\text{ }^{\circ}\text{C}$. The on-set crystallization temperature (T_{onset}) showed similar trends, but less obvious. This non-monotonous trend of the crystallization temperature dependence on the MXene loading can be explained by the competition between the nucleation and confinement effect of MXene nanoplatelets[11]: when introducing trace amount of MXene ($\sim 0.1\text{ wt.}\%$) into PEO, heterogeneous nucleation effect of MXene is dominant in the system, and T_c therefore increases. Further adding MXene into the system leads to the formation of rigid MXene network, which impose a strong confinement effect for further crystal growth, similar to the case of CNT-containing polymer nanocomposites.[11] Subsequently, the crystallization temperature decreases. Note that comparing MXEO-4 with MXEO-3, the peak temperature suffered greater depression than the onset crystallization temperature, supporting the confinement effect argument. Further increasing MXene content to 5 wt.% leads to an upshift of the crystallization temperature, indicating that at this loading, more polymers are within the surface of the MXene plates (see following discussion on the inter layer distance of an ideal MXEO system), nucleation therefore dominates the system, therefore an upshift of the crystallization temperature was observed. In addition, the crystallization exothermic peak becomes narrower for MXEO-5 as compared with

the others, further suggesting that at the highest filler content, because most of the polymer chains are in the vicinity of filler particles, the fillers therefore greatly accelerate the nucleation process. Based on the heating thermograms (**Figure 5b**), it appears that while the MXene accelerates PEO crystallization upon cooling, the melting peak and onset temperatures remain nearly constant under the present conditions, suggesting that the nanofillers do not alter the chain melting behavior.

Figure 5. Non-isothermal DSC scans of the nanocomposites during, (a) First cooling and, (b) second heating. Both scans were conducted at a rate of 10 °C/min.

The isothermal crystallization behavior of the PEO/MXene nanocomposites was also studied using DSC. The relative degree of crystallinity at time t , $X(t)$, can be defined as follows:

$$X(t) = \Delta H_t / \Delta H_{\infty} \quad (1)$$

where ΔH_{∞} is the total heat generated by the end of the crystallization process and ΔH_t is the heat generated at time t . **Figure 6** shows the DSC isothermal crystallization curves for the five samples tested at three different crystallization temperatures, T_c , of 46, 48, and 50 °C, respectively. For all the three temperatures, the isothermal crystallization peak shifts to shorter crystallization time as the MXene content increases from 0-0.5%, indicating the nucleation effect of the 2D MXene on PEO crystallization. Interestingly, further increasing MXene content from 0.5-2% leads to an upshift of crystallization time, suggesting that MXene is hindering PEO crystallization. The half crystallization time, $t_{1/2}$, and 0.1 crystallization time, $t_{0.1}$ - defined as the time for the sample to reach 50% and 10% relative crystallinity- showed similar trends, first decrease and then increase with MXene loading. The overall plot depicts a concave-up shape, with the minimum values of both $t_{1/2}$ and $t_{0.1}$ occur at the 0.5 wt.% MXene loading. This observation is consistent with the nonisothermal crystallization results, and can be explained as that the initial decrease of $t_{1/2}$ and $t_{0.1}$ is because of the nucleation effect of MXene, while the upturn with higher MXene loading is due to the confined rigid network formed by MXene. Note that the isothermal crystallization of MXEO-5 was not included in this study, because as previously discussed, at a 5 wt.% loading, most of the PEO chains are at the vicinity of the MXene surface, and the PEO crystallization is greatly accelerated. The isothermal crystallization peak therefore is difficult to resolve using the Q2000 DSC at these crystallization temperatures.

Figure 6. Isothermal crystallization behavior of nanocomposites tested herein. (a-c) Isothermal DSC thermograms at 46 °C, 48 °C, and 50 °C. (d-f) Functional dependence of $t_{1/2}$ and $t_{0.1}$ on MXene content.

Figure 7. Avrami analysis of the isothermal crystallization behavior of MXEO- δ at 46 °C, 48 °C, and 50°C. (a-c) Avrami plot and, (d-g) Plot of n (black squares, left hand y-axis) and K (blue circles right hand y-axis) vs. MXene content.

The Avrami equation:

$$X(t) = 1 - \exp(-Kt^n) \quad (2)$$

$$\log(-\ln(1 - X(t))) = n \log t + \log K \quad (3)$$

was used to analyze the isothermal crystallization process. Here n is the Avrami exponent, and K is the crystallization rate parameter. **Figures 7a-c** show the development of relative crystallinity with respect to time for three different crystallization temperatures, and **Figures 7d-f** reveal the linear portions of $\log (-\ln(1-X(t)))$ vs. $\log (t-t_0)$ plots. K and n are plotted as a function of MXene content in **Figures 7g-h**, and listed in **Tables 2-4**. Note that in Figure 7a instead of plotting t , $(t-t_0)$ — where t_0 is the least amount of time needed for crystallization to be detected using DSC— is plotted. This is done to avoid any complications introduced by differences in induction times for the different samples

Table 2. Parameters of isothermal crystallization at 46 °C.*

Sample	n	K (min ⁻ⁿ)	t _{0.1} (min)	t _{1/2} (min)	T _{m-onset} (°C)	T _{m-peak} (°C)
PEO 300k	2.45	3.61	0.47	0.76	61.6	64.8
MXEO-1	3.41	19.76	0.29	0.47	61.2	63.8
MXEO-2	3.89	194.74	0.17	0.28	61.5	63.9
MXEO-3	3.06	26.62	0.28	0.42	60.6	63.1
MXEO-4	2.34	1.98	0.47	0.86	61.1	63.5

* n : Avrami exponent; K : crystallization rate parameter; K : $t_{0.1}$; $t_{1/2}$: the time for the sample to reach 10% and 50% relative crystallinity, respectively; $T_{m-onset}$: Onset melting temperature; T_{m-peak} : Peak melting temperature.

Table 3. Parameters of isothermal crystallization at 48 °C.

Sample	n	K (min ⁻ⁿ)	t _{0.1} (min)	t _{1/2} (min)	T _{m-onset} (°C)	T _{m-peak} (°C)
PEO 300k	2.70	0.82	0.72	1.25	62.0	65.1
MXEO-1	2.84	3.88	0.45	0.73	61.6	64.1
MXEO-2	3.28	36.37	0.26	0.41	61.8	64.2
MXEO-3	2.88	5.27	0.43	0.68	61.1	63.4
MXEO-4	2.37	0.50	0.73	1.42	61.6	63.9

Table 4. Parameters of isothermal crystallization at 50 °C.

Sample	n	K (min ⁻ⁿ)	t _{0.1} (min)	t _{1/2} (min)	T _{m-onset} (°C)	T _{m-peak} (°C)
PEO 300k	2.82	0.10	1.37	2.45	62.4	65.5
MXEO-1	2.34	0.57	0.79	1.39	62.1	64.5
MXEO-2	3.28	5.98	0.43	0.68	62.3	64.6
MXEO-3	2.89	0.87	0.72	1.18	61.7	63.8
MXEO-4	2.62	0.09	1.34	2.62	62.1	64.3

Both relative crystallinity and the Avrami plot (**Figure 7a-f**) show that with increasing the MXene content in the composites, the curves first shift left, then right, indicating that crystallization rate first increases, then decreases. This can be quantified by examining the Avrami constants. At $T_c = 46$ °C, K value increases from 3.61 for PEO to 17.76 and 194.74 for MXEO-1 and 2, it then decreases to 26.62, and 1.98 for MXEO-3 and 4, respectively. Similar trends can be observed for $T_c = 48$ °C and 50 °C. This again can be attributed to the combined nucleation and confinement effects of the 2D MXene fillers, and at 0.5 wt%, the highest crystallization rate is achieved. Of interest is that the Avrami exponent n shows a similar trend, at $T_c = 46$ °C, n increases from 2.45 to 3.41 and 3.89 for MXene-1 and 2, and then decreases to 3.06 and 2.34 for MXene-3 and 4, respectively. The Avrami exponent n typically indicates the growth dimension of a polymer crystal. Note that in many cases, n also depends on other factors that complicate the situation. Such factors include growth rate changes during crystal growth, volume changes during crystallization, and nucleation mechanism changes due to asymmetric

nucleation agents, among others. The current study shows an increase from 2.45 to 3.41 and 3.89 at low MXene loading, suggesting that when more heterogeneous nucleation leads to more spherulite with smaller sizes, and at the early stage, the growth has a high dimension. As the MXene content increases to >1 wt.%, a more 2D type of growth upon the addition of MXenes (comparing to MXEO-2). In general, for semicrystalline polymer nanocomposites, n decreases slightly with the addition of nanofillers.[14] A decrease in n indicates that the growth dimension decreases with the nanofiller addition, which can be attributed to (i) the nanofiller serves as a lower dimensional template for polymer crystal growth. In this case, the initial consumption of the polymer melt follows the dimensionality of the nanofiller (2D in the present case). (ii) the confined growth of the polymer crystals due to the dense nucleation on the filler surfaces. Both factors hold in the present study, particularly at high MXene content, which can be indirectly attributed to a stronger MXene-PEO interaction due to the presence of abundant polar groups on the $\text{Ti}_3\text{C}_2\text{T}_x$ surfaces. Note that based on the mass density of MXene $\sim 3.6 \text{ g/cm}^3$, the volume fraction of MXEO-1 to MXEO-5 can be calculated to 0.033%, 0.165%, 0.33%, 0.66% and 1.65%.[39] Assuming that the MXene nanoplatelets are $\sim 5 \text{ nm}$ in thickness, the average distance between two adjacent MXene nanoplatelets are therefore $\sim 15 \mu\text{m}$, $3 \mu\text{m}$, $1.5 \mu\text{m}$, $0.7 \mu\text{m}$ and $0.3 \mu\text{m}$, respectively. For MXEO-1 and 2, the distance is relatively large and 3D growth was observed. In MXEO-3 and 4, the growth is obviously confined within the 2D space, and therefore n decreases.

Conclusions

In summary, 2D $\text{Ti}_3\text{C}_2\text{T}_x$ nanoplatelets - produced by etching a Ti_3AlC_2 powder in a solution of lithium fluoride and 6 M HCl – approximately $88 \times 88 \times 5 \text{ nm}^3$, were used to

fabricate $\text{Ti}_3\text{C}_2\text{T}_x$ /PEO nanocomposites with MXenes contents that varied from 0 to 5 wt.%. The crystalline structure of PEO did not change with the addition of MXene as evidenced by the WAXD experiments, which also showed that the 2D MXene layers were exfoliated. Both nonisothermal and isothermal crystallization study showed that with addition of MXene, crystallization rates first increased and then decreased. The fastest crystallization rate was observed at 0.5 wt% MXene content. This was attributed to the competition of nucleation and confinement effect of the 2D filler: at low MXene loading, the 2D filler accelerate PEO crystallization due to heterogeneous nucleation. With increasing MXene content to 1-2 wt%, the 2D nanofillers provide a rigid confinement network, which slows down the crystallization. At MXene content of ~ 5 wt%, PEO crystallization increases again, because that most of the polymers are in the vicinity of the nanofiller surface, and the confinement effect therefore is not significant. Future study will focus on the use of these nanocomposites as PEO-based solid polymer electrolytes.

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Table of Content

Structure and Crystallization Behavior of Poly(ethylene oxide)/Ti₃C₂T_x MXene Nanocomposites

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