Research Article

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Natural rubber latex/MXene foam with robust and multifunctional properties

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Abstract: Low strength has always been one of the main factors limiting the application of foams. We acquire a natural rubber latex/MXene foam composite with high strength and versatility by adding MXene to the natural rubber latex. It is shown that natural rubber latex foam (NRF) with 2 and 3 phr of MXene shows obviously enhanced tensile strength by 171% and 157% separately as compared to that of neat NRF. Furthermore, the composite also has better electrical conductivity and electromagnetic shielding than NRF, which can be used in the automotive industry, aviation industry, and many other aspects.

Keywords: natural rubber latex foam, MXene, tensile strength, electrical conductivity, electromagnetic shielding

1 Introduction

Due to the advantages of low relative density, high specific strength, and large specific surface area, foam has been extensively studied by researchers in recent years (1–8). For example, natural rubber latex foam (NRF) has attracted wide attention because of superior performance, such as excellent elasticity, lightweight, and so on (9–15). However, the mechanical strength of NRF is low and function of NRF is relatively single, which seriously limits its scope of use. Researchers enhance the mechanical properties of NRF by filling rice husk (16), kenaf core (17), eggshell (18), and imparting antimicrobial properties to NRF via zinc oxide nanoparticles (19), silver nanoparticles (20–22), and chitin (23). For instance, Ramasamy et al. incorporated rice husk powder (RHP) into NR latex compound, and the hardness of RHP-incorporated NRF increases with increasing RHP filler loading (24). In addition, Bashir et al. have demonstrated that the tensile strength of NRF filled with eggshell power initially drops at low eggshell powder filler loading and then increases with the increment of filler loading from 5 to 10 phr (18). Moreover, Zhang and Cao have used the natural antibacterial agent chitin as a loading filler, environmentally friendly and antibacterial NRF was prepared herein (23). However, in recent progress, to the best of our knowledge, few studies realize both versatility and mechanical strength for the foam. Thus, it is a challenge to expand its application scope and improve its mechanical properties at the same time.

MXenes, a new family of 2D materials, were discovered by scientists of Drexel University in 2011 (25). The general chemical formula of MXenes is expressed as $M_{n1}X_nT_x$, where M is a transition metal (Ti, Mo, Cr, Ta, etc.), $X$ is C or N, and $T_x$ is a surface termination function (−OH, −O, or −F), $n = 1, 2, or 3$ (26,27). High-concentration etchant containing hydrofluoric acid and sodium 1-ascorbate is used to prevent oxidation (28). In particular, its wide surface area and metallic properties make MXenes possess excellent properties in functionalized materials, such as energy conversion and storage (29,30), thermoacoustic devices (31,32), electromagnetic shield (33–35), and so on.

In this study, natural rubber latex/MXene foams (NRMFs) are prepared by Dunlop processes. MXene is uniformly dispersed in NRF and NRMF shows excellent properties. For example, NRF with 2 phr of MXenes shows higher tensile strength of 0.60 MPa more than cure NRF of 0.35 MPa. Moreover, nanocomposites also possess...
electrical conductivity and electromagnetic interference (EMI) shielding performances and NRMF composites could be widely applied to automotive industry, aviation industry, and many other aspects for future applications. This work provides a good guide toward the design of NRF with excellent mechanical and multifunctional properties.

2 Materials and methods

2.1 Materials

Titanium aluminum carbide (Ti3AlC2) was supplied by 11 Technology Co. Ltd., Changchun, China. Lithium fluoride (LiF, AR, 99%) and hydrochloric acid (HCl, 36.0–38.0 wt% in H2O) were purchased from Aladdin Reagent Co. Ltd., China. High ammonia (HA) natural rubber latex (60%) was supplied by China Hainan Rubber Industry Group Co., Ltd. Potassium oleate and sodium silicofluoride were purchased from Aladdin. Zinc oxide, sulfur, 1,4-dibenzyloxybenzene, and 2-mercaptobenzothiazole were of industrial grade.

Figure 1a shows composite foam preparation. A total of 1.0 g of Ti3AlC2 powder was gradually added to the etchant that was prepared by adding 1.8 g of LiF to 20 mL of 9 M HCl and left under continuous stirring for 5 min, and the reaction was allowed to run for 35 h at 45°C. The acidic mixture was washed with deionized H2O via centrifugation (6 min per cycle at 3,500 rpm) for multiple cycles until pH 5 was achieved. The centrifugal product was sonicated for 0.5 h and then filtered by vacuum to obtain the film. Finally, dry it in vacuum at 100°C for 24 h. Ammonia concentration in HA latex was reduced to 0.20–0.25% by stirring, then 2.5 g sulfur, 1.5 g 2-mercaptobenzothiazole, and 1.5 g zinc diethyl dithiocarbamate were added to natural rubber latex with 100 g dry rubber content. The composite latex was stirred for 1 h and then stored for 24 h to make it fully prevulcanized. A total of 10 g of 10 wt% potassium oleate solution and MXene (0, 1, 2, 3, 4, 5 wt%) were added to the composite latex to reach four times its original volume. The gelled foam is cured by 2.5 g of zinc oxide and 1.5 g of sodium silicofluoride, then vulcanized in an oven at 120°C for 25 min. Finally, it was washed with deionized water to remove residual reagents and dried at 50°C for 2 h. We denote NRF with MXene as NRMF-x, where x is the weight fraction of MXene.

2.2 Characterization

MXenes were characterized with a Rigaku Smart Lab X-ray diffractometer (XRD). The scanning range of XRD is 10–90°, and the scanning speed is 5° per minute. The morphology and microstructure of Ti3C2Tx sheets and nanocomposite were observed with scanning electron microscope (SEM, Verios G4 UC) at a low acceleration voltage of 3 keV at room temperature. Prior to examination, samples were gold sputter coated to render them electrically conductive. Transmission electron microscope (TEM) images for samples were obtained on FEI Talos F200C TEM at an accelerating voltage of 200 kV. Ultrathin sections for TEM were prepared by a Leica EM FC7 ultramicrotome with a diamond knife at −60°C.

Zeta potentials of composite latex were determined by a Zeta sizer Nano S90 (UK). Mechanical properties of samples were measured using GOTECH AI-3000 testing.
Uniaxial tensile measurements were performed at room temperature with a strain rate of 100 mm/min. The specimen was a dumbbell-shaped thin strip with central dimensions of $25 \times 5 \times 3$ mm. Dynamic mechanical properties were measured in tensile mode on a TA Instruments Q800 with a gas cooling accessory under a nitrogen atmosphere for the determination of glass transition temperature ($T_g$) and storage modulus ($E'$). The dimensions of the specimens tested were $12 \times 5 \times 3$ mm. The $T_g$ and $E'$ were determined at a heating rate of 1°C/min and a frequency of 1 Hz. $T_g$ values were measured by taking the maximum in the loss tangent ($\tan \delta$) as the $T_g$ values. In all cases, a preload force of 0.01 N was applied. The temperature range was from $-100^\circ$C to $0^\circ$C. Differential scanning calorimeter (DSC) curves of samples were obtained on TA Instruments Q100 under a nitrogen atmosphere. The temperature range was from $-70^\circ$C to $0^\circ$C, and the heating rate was 10°C/min. The EMI shielding performance was analyzed by a AGILENT E5071C within the frequency range of 8.2–12.4 GHz and the dimensions of the specimens tested were $23 \times 10 \times 2$ mm. Electrical conductivities of nanocomposites were measured with a 4-probe Tech ST-2253 resistivity meter at room temperature and the dimensions of the specimens tested were $12 \times 5 \times 3$ mm.

### 3 Results

#### 3.1 Structure characterizations

The structure evolution of Ti$_3$C$_2$T$_x$ sheets is observed through morphological observation and XRD scanning. The removal of the Al layer causes the (002) peak to move from 9.68° of Ti$_3$AlC$_2$ (JCPDS No. 52-0875) to 5.56° of Ti$_3$C$_2$T$_x$ (Figure 1b). The interlayer spacing increase and the tightly packed Ti$_3$AlC$_2$ (Figure 2a) are transformed into a loose-layered structure (Figure 2b–d).

The preparation of NRMF is achieved by forming a uniform dispersion of Ti$_3$C$_2$T$_x$ and NR. As shown by the Zeta potential (Figure 3a), a uniform NR/Ti$_3$C$_2$T$_x$ dispersion is formed. Figure 3b and c show cross-section photographs of cure NRF and NRMF-1. Although foam composed of non-uniform cell size with irregular shape, generally, the holes are evenly distributed. Through SEM and TEM, the overall distribution of MXene sheets in NR was verified (Figure 3d–h). Taking NRMF-3 as an example, the minimum layer spacing is 1.59 nm of MXene, which is shown in the inset in Figure 3h. In addition, the bright outline in the energy-dispersive spectroscopy (EDS) element mapping is consistent with the distribution of the Ti and F elements in
MXene, and the light-colored area is the natural rubber mainly containing C and O elements (Figure 3i).

### 3.2 Mechanical properties of NRMF

Due to their porous structure, polymer foam materials often possess excellent elasticity and poor mechanical properties. When the expansion ratio is four times, the thickness is compressed to 50% for 22 h, and the recovery thickness after compression is tested to characterize its rebound rate. After adding MXene, excellent elasticity of NRMF is still maintained, as shown in Table 1. Figure 4a depicts the typical stress–strain curves of NRMF. Happily, MXene shows a significant enhancement effect on NRF. Specifically, compared with pure NRF (0.35 MPa), the tensile strengths of NRMF-2 (0.60 MPa) and NRMF-3 (0.55 MPa) are significantly increased by 171% and 157%. At the same time, the percentage of breaking elongation of the samples increased from NRF (645%) to

<table>
<thead>
<tr>
<th>NRMF sample</th>
<th>NRF</th>
<th>NRMF-1</th>
<th>NRMF-2</th>
<th>NRMF-3</th>
<th>NRMF-4</th>
<th>NRMF-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial thickness (mm)</td>
<td>15.8</td>
<td>14.2</td>
<td>14.7</td>
<td>15.6</td>
<td>14.8</td>
<td>15.0</td>
</tr>
<tr>
<td>Compressed thickness (mm)</td>
<td>15.1</td>
<td>13.6</td>
<td>13.9</td>
<td>14.9</td>
<td>14.0</td>
<td>14.2</td>
</tr>
<tr>
<td>Resilience rate (%)</td>
<td>95.7</td>
<td>95.8</td>
<td>94.6</td>
<td>95.5</td>
<td>94.6</td>
<td>94.7</td>
</tr>
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NRMF-3 (689%), and the elasticity of the sample was further improved. However, although NRMF-4 and NRMF-5 have improved compared with pure NRF, the comparison between NRMF-2 and NRMF-3 has declined. Due to the nanosheet structure of MXene, we believe that as the number of additions increases, its agglomeration in NRF affects the further improvement of performance. $T_g$ of NRMF-2 reaches the highest temperature, at which MXene limits the movement of rubber networks (Figure 4b).

To further resolve the changes in molecular structure network, dynamic mechanical analyzer is used to obtain the temperature dependence of storage modulus ($E'$) and loss factor (tan $\delta$) curves. NRMF-2 (4,008 MPa) and NRMF-3 (2,606 MPa) storage modulus are greatly improved compared to NRF (923 MPa), as shown in Figure 5a. Another important phenomenon is that tan $\delta$ peak of samples shifts toward higher temperature, such a $T_g$ changing trend of NRF ($-56.1^\circ C$) to NRMF-2 ($-55.3^\circ C$) and NRMF-3 ($-55.7^\circ C$) is consistent with DSC results (Figure 5b).

### 3.3 Electrical and EMI shielding properties of NRMF

With the increasing use of electronic devices and rapid expansion of telecommunication networks, for polymer nanocomposites with excellent flexibility, it is very necessary to have EMI shielding applications to expand their scope of use. The layered network of MXene is conducive to multiple scattering and interface polarization of incident electromagnetic waves. The incident waves can be mostly dissipated and attenuated, which significantly increases the absorption contribution. NRMF-2 and NRMF-3 conductivities are two orders of magnitude higher than that of NRF, and EMI shielding is also

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**Figure 4:** (a) Representative stress–strain curves. (b) DSC heat flow curves of samples.

**Figure 5:** (a) Temperature-dependent curves of storage modulus ($E'$) and (b) temperature dependent curves of tan $\delta$. 

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significantly improved in Figure 6. With the increase in the number of MXenes added to the natural rubber latex, the NRMF performance decreases due to agglomeration.

4 Conclusions

In this article, robust and multifunctional composites of NRMF are prepared by Dunlop processes. Consequently, compared with pure NRF, the tensile strengths of NRMF-2 and NRMF-3 are significantly increased by 171% and 157%, $T_g$ increases by about 0.8–1°C. Moreover, nanocomposite foaming shows the electrical conductivity of $6.18 \times 10^{-4}$ Sm$^{-1}$ and an EMI shielding performance of 6.0 dB with NRMF-2. This work provides a simple way to manufacture high-strength elastic foams with electrical conductivity and EMI shielding capabilities, which expands the potential applications of natural latex foam materials.

Author contributions: Ya-Dong Yang: investigation and writing – original draft; Gui-Xiang Liu: investigation; Yan-Chan Wei: formal analysis; Shuangquan Liao: resources and writing – review and editing; Ming-Chao Luo: conceptualization, writing – original draft, and writing – review and editing.

Conflict of interest: The authors declare no competing financial interests or personal relationships that could have appeared to influence the work reported in this article.

References


