

# Influence of Interpenetrating Polymer Networks (IPN) Microstructure on Underwater Acoustic Stealth Performance

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**Abstract:** According to the configuration and absorption theory of polymer macromolecule materials, a kind of IPN with wider temperature range and higher damping property was designed and synthesized. By using the spectrum of dynamic mechanical thermal analysis (DMTA) and acoustic pulse tube device, the microstructure, phase separation degree, phase size and phase continuity of IPN with different components were analyzed. The experimental results show that the nano size grade of phase, the continuous and homogeneous IPN phase can provide higher absorption coefficient. The absorption coefficient of optimized sample I09 is 0.7 in 2 kHz, and the absorption peak is 0.9 in 4 kHz. Then the underwater acoustic properties of modified IPN filled with mica, micro-balloon and nano-SiO<sub>2</sub> were discussed respectively to indicate that the inhomogeneous property of filler-modified IPN can improve the underwater acoustic stealth performance effectively, and the micro size grade of these filler-modified IPN can work well in low frequency acoustic stealth.

**Key words:** interpenetrating polymer networks (IPN); polyurethane; damping; absorption coefficient; fillers

## 1 Introduction

Generally speaking, the main characteristic of submarines is to provide secluded capability and gusty attack. So, reducing the underwater acoustic target strength of submarines will effectively shorten the detectable distance and enhance survivability of home submarines. With the rapid development of detective sonar and enhancement of cruise depth, some new challenges are brought to acoustic stealth of submarine. Nowadays, the focus of underwater absorbing material is shifting to compression resistance, low frequency and wide band absorption. This implies that the second anechoic tile based on the materials of macromolecule polymer becomes an active topic of underwater acoustic stealth<sup>[1-4]</sup>.

Interpenetrating polymer networks (IPN) is a new synthetically macromolecule composing two or more polymers with a physical circle connected by a cross

network. Compared with simple mixed polymers, block polymers, and inarched polymers, IPN is characterized with interspace topology structure. When the sound wave transits macromolecule coating, energy will be transferred to the chains and trigger relative internal friction movement of chains transform and absorb the energy<sup>[5-7]</sup>. The loss factor of polymer can be enhanced by adding some kinds of fillers, such as mica, micro-balloon and nano-SiO<sub>2</sub>, into polymer. Meanwhile, the absorption coefficient can be improved accordingly. Current researches seldom focus on dynamic mechanical thermal analysis (DMTA) and underwater acoustic performance of filler-modified IPN<sup>[8-10]</sup>. So our study on IPN and the microstructure of modified IPN was addressed to investigate the influence of DMTA and underwater acoustic stealth properties.

## 2 Experimental

### 2.1 Molecule design and synthesise of IPN

It's well known that there are some relations between the damping theory of IPN and the dynamic stress relaxation. The nature of damping is that, the inner stress

wave of material can be produced in the alternation stress field, and then molecule movement of some modes is inspired to cause loosen fluctuate of the polymer networks. Consequently, the internal friction produced by displacement and reversion of networks will transform mechanical energy into heat energy and provide mechanical damping peak. In the polymer networks, the damping area is directly proportional to the quantity of specifically element. Therefore, the high damping IPN depends on not only the larger loss factor area (LA value) of polymer materials but the solubility parameter of each component to leverage its compatibility. In addition, the greater difference of the vitrification transformation temperature ( $T_g$ ) between components will expand damping area.

The molecule chain of polyurethane (PU) is very active, and its molecule structure can be designed flexibly. Then different PU damping can be synthesized by importing branched chain, controlling the length of main chain and changing cross linking. So PU can be identified as one of IPN components, and the epoxy resin (EP), unsaturated polyester resin (UPR) and polyorganosiloxane dimethyl siloxane (PDMS) are the candidates of experiments. EP is a kind of excellent hot setting materials with nicer mechanical and caking property. There is a benzene ring in the main chain of bisphenol EP, which can be used to improve damping in high temperature. Hence, the transformation temperature of  $T_g$  is higher than the one of PU. UPR is another popular application material which is characterized with high active reaction, low viscosity and well corrosion resistance and machining techniques. What's more, the solubility of UPR is very close to the one of EP, so the IPN generated from PU/UPR is capable of well damping property. As for PDMS, it can provide oxidation inhibition, weathering resistance, temperature independency, which can cut down internal stress as well as enhance the tenacity of EP<sup>[11,12]</sup>. Especially, PDMS can also improve heat hardness and low damping properties of PU.

## 2.2 Dynamic mechanical thermal analysis

According to micro-phase separate thermodynamics theory of IPN, it is difficult to construct a kind of homogeneous and steady material on the basis of IPN architecture. However, lots of IPN have been developed and widely used in industry and social life. The corresponding reason can be addressed from two aspects. On one hand, during the reaction process of synthesizing IPN, increasing molecular weight aggravates phase separation to create a multiphase structure. On the other hand, molecular weight is growing dynamically, in which migration of chain must be hampered by chain gravitation and

entwisting network. These two factors can work together to reach non-thermodynamics equilibrium, whose degree of phase separate is much lower than the one of common admixture<sup>[13]</sup>. As a result, the specified microstructure of IPN is mostly influenced by reaction dynamic parameter. Then DMTA can be used to measure the modulus,  $T_g$ , and damping responded by temperature, time and frequency, etc. In general, the acoustic parameters of IPN residing in 0.5-60 kHz can be generated from 1-100 Hz by time-temperature equivalence of high viscoelasticity polymer.

## 2.3 Scan electron microscope analysis

The mechanical and damping properties of IPN lie on its microstructure. At present, the most popular method for analyzing microstructure is to get micrographs of IPN samples with electron microscope. In this way, the SEM micrographs can be used to analyze the nature of IPN in a quality manner. In this paper, microstructures of IPN samples are characterized with the following steps: to put the IPN samples in the liquid nitrogen for 20-40 minutes, cut them off in lower temperature, and then dry the samples in vacuum with room temperature for 4 hours; to sprinkle gold in the fresh cutting surface, then scan and photograph the microstructure in the S-570 SEM.

## 2.4 Underwater acoustic response

The underwater acoustic response can be directly obtained from acoustic pulse tube device test, as Fig.1 shown. It is mainly adopted by small-scale samples. More specifically, the absorption coefficient and reflection coefficient can be calculated by the crest value and phase of reflected wave when the tested IPN samples reside in the boundary condition of soft backing and rigid backing. In Fig.1, the thickness of IPN sample is 50 mm.

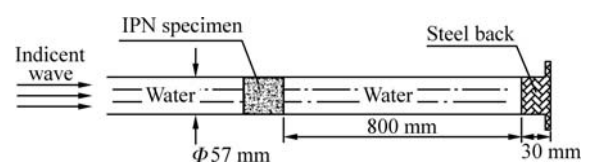


Fig.1 Acoustic pulse tube device

# 3 Results and Discussion

## 3.1 The DMTA and microstructure of IPN in different components

In this section, some IPN samples will be synthesized in equal mass ratio. They are I01: PU/EP/UPR, I02: PDMS blocking PU/EP/UPR and I03: PDMS inarching PU/EP/UPR. Fig.2 shows the corresponding DMTA spectra respectively. It implies that the PU/EP binary IPN can broaden the damping area. The damping in high temperature is derived from the internal friction movement of big benzene ring in bisphenol epoxy chain, and the one in low temperature is derived from the pliancy of

polyether chain. UPR is imported here to expand the damping areas and improve the compatibility of components. Fig.2(a) shows the wider damping properties of the single peak.

To import PDMS for multipleunit IPN of PU/EP/UPR/PDMS can expand the damping area, especially under  $-50\text{ }^{\circ}\text{C}$  because of the pliancy chain. The PDMS blocking PU/EP/UPR performs serious phase separation, and shows double  $T_g$  in Fig.2(b). The main reason is that the solubility of PDMS is quite different from the PU, EP and UPR. So the blocked PDMS can not spread around the networks, and the chain of PDMS can not interpenetrate the IPN to produce a larger phase, just as the macroscopical phase separation presented by I02.

The PDMS inarching PU/EP/UPR can perform better solubility. Fig.2(c) shows the single  $T_g$ , large loss factor and wide damping area of I03. Different from I01 and I02, here only one end of inarched PDMS is linked with the main chain of PU, which makes PU chain more active. When it is inspired by acoustic wave, the chains of inarched PDMS are easier to friction with rigid chains of EP and UPR to improve the damping properties.

Especially, to discuss influence of damping caused by the micrograph of IPN, Fig.3 shows the SEM images of IPN samples with different ingredients. It means that the phase size of I02 is in micro grade, and the phase sizes of both I01 and I03 are in nano grade. So we can conclude that the DMTA spectrum will perform single  $T_g$  and wide damping areas by reducing the IPN phase size. In the contrary, the inhomogeneous phase becomes more obvious in the larger phase size areas.

Fig.3(a) illustrates the homogeneous microstructure of I01 in  $5\text{ }\mu\text{m}$  level. In this figure, the cutting surface is featured with toughness rupture, but there is no phase separation with the blurry phase boundary and the transition region of phase is wider to present continuous microstructure. This leads to the fact that PU/EP/UPR can form interpenetrating topological networks, which are different from the microstructure of common mixed polymer. It can be explained from two aspects. On one hand, the adopted technique is synchronal interpenetrating. On the other hand, the light molecular weight of MDI chain is deemed as the rigid component of polymer and bisphenol epoxy chain is the corresponding pliable component. More specifically, MDI can be treated as the solvent here in this section. Then, continuous phase can be constructed based on polymer chain, which is consistent with the result of DMTA.

Fig.3(b) shows that the phase size of I02 with blocked PDMS is in micro grade, and its separate microstructure is inhomogeneous. This is caused by the fact that the solubility of PDMS is different from other components and the rich areas of PDMS can not be dissolved by the others. So the continuous bigger phase of I02 indicates the macroscopical properties, including the double  $T_g$ , depressed mechanical property and practicability. Fig.3(c) shows the microstructure of I03 inarched by PDMS. In this figure, the phase boundary of I03 is clear and the phase size is smaller than I02's because the chain of PDMS crimps to form an independent microstructure during the process of interpenetrating polymer chains.

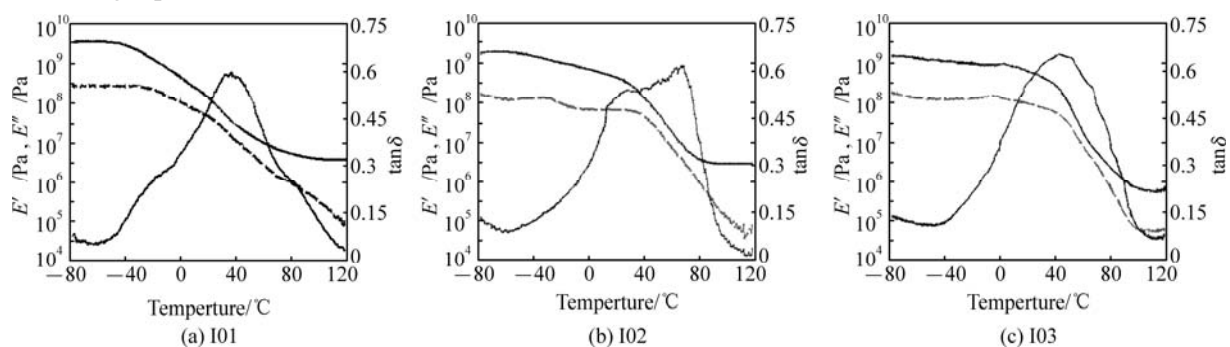


Fig.2 The DMTA spectra of IPN samples with different components

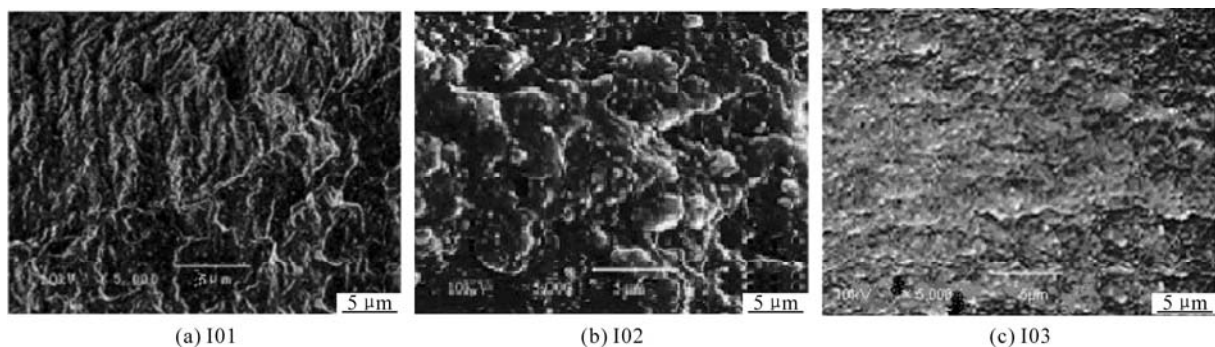


Fig.3 The SEM images of IPN samples with different components

### 3.2 Influence of IPN microstructure on underwater acoustic stealth

The samples of I04-I08 were synthesized by different components of PU/EP/UPR. Then I09 could be synthesized by the optimized results of previous multiple regression analysis. The microstructures of I04-I09 in Fig.4 are different, which leads to the difference in frequency response of absorption and reflection coefficient (Fig.5).

The microstructure of I04 in Fig.4(a) is homogeneous and its phase size is in micro grade. This means that when the frequency is higher than 2 kHz, the absorption coefficient is more than 0.6. Compared with I04, the phase of I05 in Fig.4(b) is larger and without clear phase separation, but it becomes less homogeneous. Then, the absorption peak of I05 should move towards higher frequency and its absorption coefficient in low frequency is cutting down. As for I06 in Fig.4(c), there are several

special "island" structures, and the phase size is between nano and micro grade. This implies that the microstructure of I06 can establish interpreting networks. Due to the different sizes of microstructures, I06 can provide better absorption properties. That is, the absorption coefficient is up to 0.7 when the frequency is in 2 kHz, and the absorption peak should move towards lower frequency. The microstructure of I07 in Fig.4(d) is similar to the one of I05. However, I07 has a smaller inhomogeneous phase size and better acoustic properties. The phase size of I08 in Fig.4(e) is about 5  $\mu\text{m}$  and there are some separation phase. So it is adhered to the lowest absorption properties. Relatively, Fig.5(b) shows that the reflection coefficients of I06 and I07 are lower because of homogeneous microstructure without phase separation, and the one of I05 is higher due to inhomogeneous microstructure.

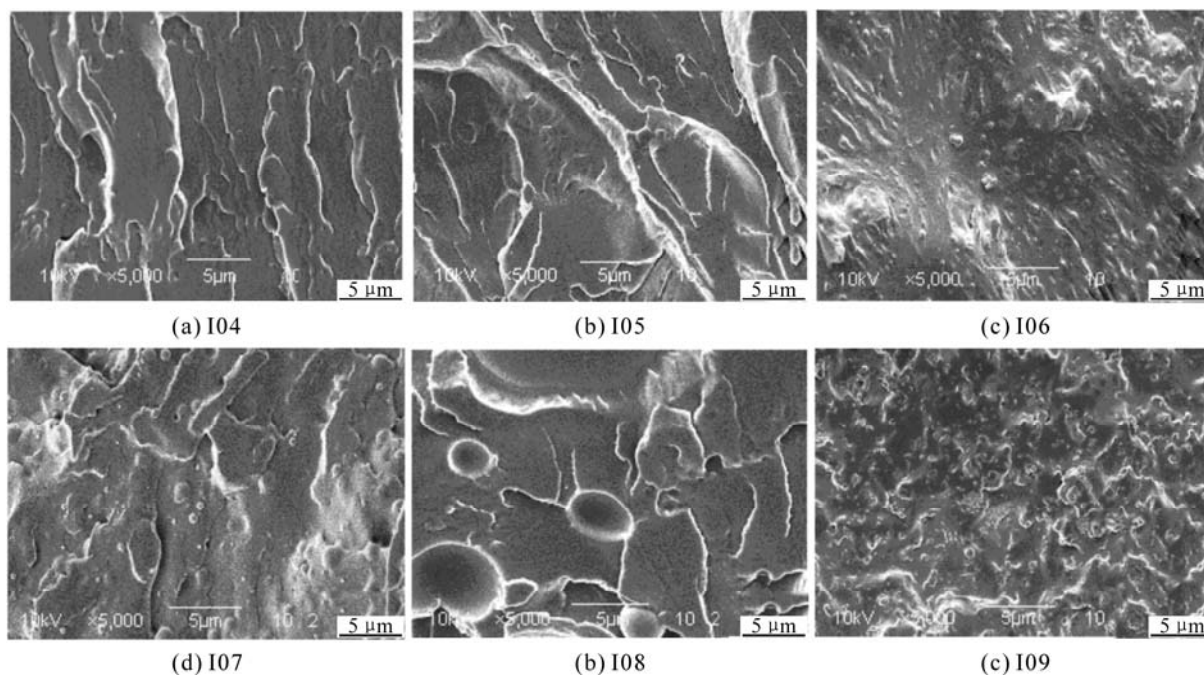


Fig.4 The SEM images of IPN samples

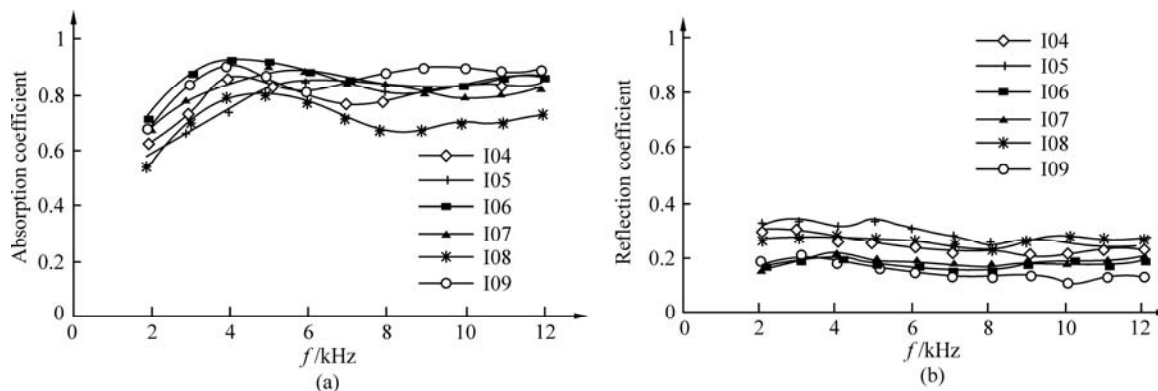


Fig.5 The acoustic performance of IPN samples

The optimized sample I09 represents better acoustic stealth properties than the previous 5 samples. In detail, the absorption coefficient is 0.7 in 2 kHz, the absorption peak is 0.9 in 4 kHz, and the reflection coefficient is below 0.2 within the range of experimental frequency. The continuous phase size of I09 in Fig.4(f) resides in hundreds nm level, and its microstructure is a kind of symmetrical interpenetrating “island” structure. It can be concluded that the continuous and homogeneous phase, whose size is in nm grade, can improve the underwater acoustic stealth of IPN effectively.

### 3.3 Influence of microstructure of filler-modified IPN on underwater acoustic stealth

The fillers can break the molecular force except for the bond gravitation to increase internal friction. Meanwhile, these fillers can vibrate together with the expansion and compression of networks in the sound wave. This result can enhance the efficiency of lagging absorption. Table 1 shows the performance parameters of IPN with the fillers as mica, micro-balloon and nano-SiO<sub>2</sub>. With decreasing granularity in the same percentage of fillers, the damping peak moves toward higher temperature, and the valid damping temperature area ( $\Delta T$ ,  $\tan \delta > 0.3$ ) is expanded. Fig.6 shows that the transitional boundary surface between fillers and basal body becomes larger when the surface area ratio increases. So the increased percentage of phase separation can not only help merge those components, enhance the integrity and make them homogeneous, but link  $T_g$  between fillers and basal body to reach a wider damping peak. Therefore, IPN with mica

fillers can produce less phase boundary with a high damping peak and a narrow  $\Delta T$ . And IPN with nano-SiO<sub>2</sub> fillers will generate a lower damping peak and a wider  $\Delta T$ .

**Table 1 The performance parameters of IPN with different fillers in different sizes**

Filler	Percentage	Granularity	Tan $\delta$	$T_g/^\circ\text{C}$	$\Delta T/^\circ\text{C}$
Mica	8%	60 mesh	0.92	43.1	65.3
Micro-balloon	8%	80 mesh	0.67	14.2	98.5
Nano-SiO <sub>2</sub>	8%	20 nm	0.64	64.8	94.5

Fig.7 suggests the acoustic experimental results of IPN with different fillers. It concludes that compared with other fillers, the absorption coefficient can be improved greatly by modifying mica and its characteristic absorption peak moves towards lower frequency, as Fig.7(a) illustrated. The reason is that the properties and microstructures of fillers are different in sheet shape, micro-perforated and hollow structure, which can improve the damping property of IPN. These characteristics can strengthen the internal friction between IPN chain and these fillers in sound wave. In particular, the tropism sheet mica can transform some compression waves into shear wave by partial inhomogeneous features. Concerning the fillers such as micro-balloon and nano-SiO<sub>2</sub>, they can be used to provide better absorption and modulus to IPN<sup>[14]</sup>. Fig.7(b) shows the reflection coefficient increased by mismatched impedance of inorganic fillers. Therefore, when considering the absorption and reflection properties, it is recommended to choose sheet mica and micro-balloon as the desirable fillers. If so, the acoustic structure of IPN should be optimized to reduce the reflection.

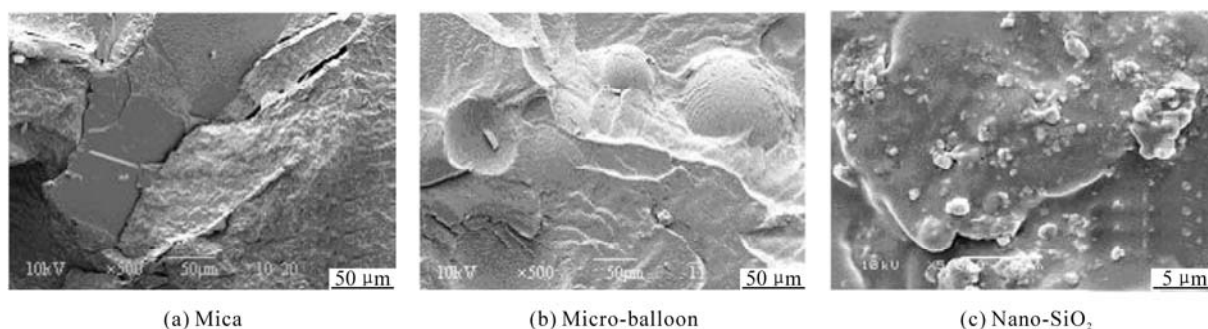


Fig.6 The SEM images of IPN samples with different fillers

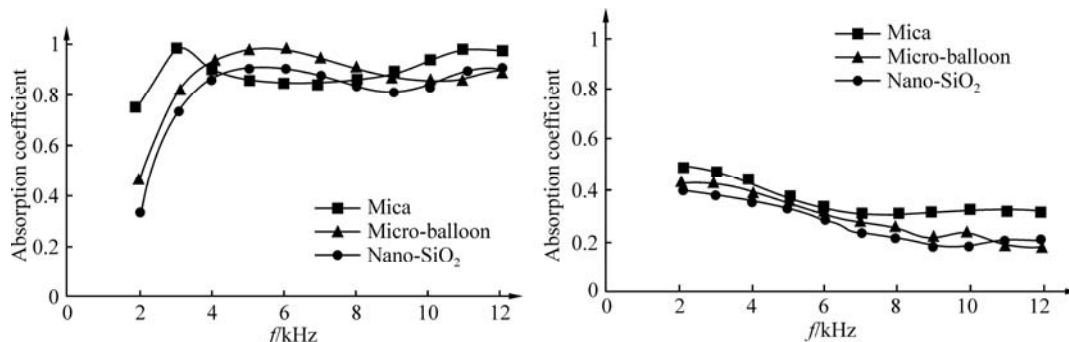


Fig.7 The acoustic performance of IPN samples with different fillers

## 4 Conclusion

The microstructure of IPN provides better compatibility of components. The phase size of IPN inched by PDMS becomes smaller, and the phase boundary is much clearer. There is a great diversity in the phase size of IPN synthesized with different percentages of PU/EP/UPR. The IPN with nm grade phase size and continuous phase boundary can work well in underwater acoustic stealth; on the contrary, the IPN with micro grade phase size and serious phase separation only offers lower underwater acoustic stealth performance. The filler-modified IPN can improve the underwater acoustic stealth performance. Particularly, the IPN filled with sheet mica provides better underwater acoustic stealth performance in low frequency.

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