Novel CNT-polymer Nanocomposites used in Oilfield for High Pressure, High Temperature Sealing System

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ABSTRACT

A novel sealing system base on MWNT (multiwalletd carbon nanotubes) and polymer nanocomposites was developed for the use in the exploration and development of hotter, deeper reservoirs. Fully dispersed and better bonding are two critical advances that enhance its mechanical properties. We solved the critical issues in 2008, and developed a novel sealing system for high pressure, high temperature reservoirs. After many successful field tests around the world, the new system was released for the oilfield. It marks a rare success story for the use of nanotechnology in energy resources.

Keywords: carbon nanotubes, oilfield, sealing system, nanocomposites, high pressure, high temperature (HPHT)

1 INTRODUCTION

Hydrocarbons such as oil and gas are critical resources for the functioning of human societies. To avoid another energy crisis, it is essential to increase oil extraction. Today, with the dearth of easy-to-reach reservoirs, the oil and gas industry is conducting more of its exploration and exploitation activities in difficult-to-reach and harsh environments. Key challenges in exploiting these new reservoirs include extremely high temperatures, high pressures, and associated sealing issues. We are using MWNT (multiwalled carbon nanotube) nanocomposites in the development of a high pressure, high-temperature (HPHT) sealing system for extracting hydrocarbons in these harsh environments. The new sealing solution has been successfully tested around the world. This paper clarifies our "cellulation" technologies and the resulting fundamental changes as well as the significant improvements in material properties that enabled the development of this new sealing solution for harsh environments and high temperatures.

2 NANOCOMPOSITES FOR ENERGY

2.1 Target: HPHT Reservoirs

Fig. 1 shows a cross-sectional image of an oilfield. Most conventional sealing systems limit operations to 350°F (175°C) and 20,000 psi **[1, 2]**, which allows exploitation only in typical shallow reservoirs. To reach the proven supplies of untapped oil and gas that are in deeper and hotter reservoirs, the industry needs reliable sealing systems with capabilities that exceed 500°F (260°C) and 35,000 psi **[1, 2]**. With today's technology the average worldwide recovery ratio of oil and gas is about 35% **[3]**. This means we are not able to access and produce approximately 65% of known reserves using conventional technology. Through innovation and new technology development, the access and recovery rates can possibly be increased from 35% to 70% or more **[3]**, meaning that we can potentially double oil and gas recovery.

Technology is the key to accessing these deeper and hotter reserviors. Reliable sealing is critical for enabling operations in these conditions. Another sealing challenge comes from reserviors located in offshore and deepwater areas. For operations in such areas, seals must perform well in cold seabed temperatures that average 40°F (**Fig. 1**) while maintaining integrity in the HPHT conditions of the reservoir. Thus, a critical sealing technology that can handle both high temperatures and low temperatures is essential for accessing and operating in deepwater and HPHT reservoirs.

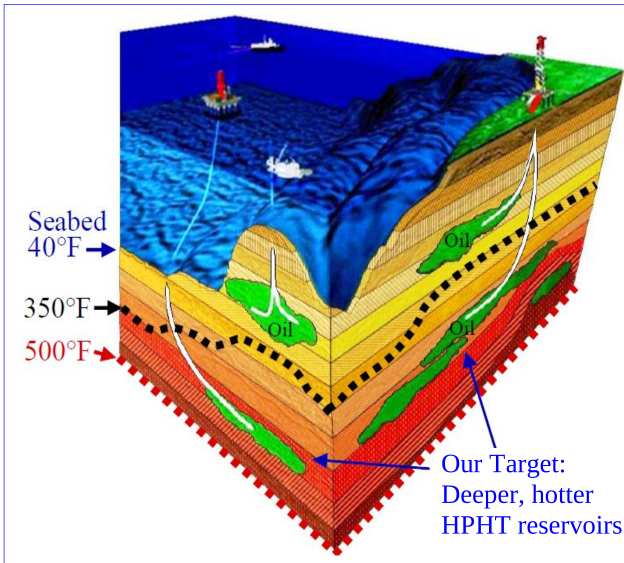

Fig. 1: Underground oil reservoirs on land and offshore requiring a novel sealing systems for high pressures and temperatures from 40°F (4°C) at seabed up to 500°F (260°C) in hotter reservoirs.

2.2 Background of Nanocomposites

Since the discovery of carbon nanotubes in 1976 (by Endo et al.) **[4]** and the development of mass production techniques for MWNTs in 1988 **[5]**, numerous efforts in academia and industry have tried to use MWNT to enhance the properties of polymeric materials **[6, 7]**. Two significant challenges were identified, namely the dispersion of MWNT in the polymer matrix and bonding between MWNT and the polymer matrix **[6, 7]**. We respectively addressed these critical issues by developing two key technologies: "cellulation" to fully disperse the MWNT homogeneously and a specialized treatment processes to optimize the surface conditions of MWNT for optimal bonding with the matrix **[8 – 10]**.

3 RESULTS AND DISCUSSION

3.1 Cellulation Technology

Fig. 2 shows the reinforcing effect of the CNT (carbon nanotubes) percentage on a polymer. The back and red lines show the storage modulus (***E′***) of pure polymer and composite respectively with 2.7% MWNT from –50°F to 750°F (–45°C to 400°C). Both become softer at high temperature. The blue line (15.5% CNT) and green line (8.4% CNT) show the ***E′*** is stronger until 750°F from the high concentration of CNT nanostructure.

Fig. 3 shows the relationship between the reinforced effect (***E′***) and CNT concentration at different temperatures from same test results in **Fig. 2**. Below 8.4% CNT, the reinforced effect is smaller at all temperatures. In higher concentration, the reinforced effect increases. The problem is how to fully disperse the CNT up to a high concentration. These results are consistent with those reported by L. Bokabze **[6]**.

Fig. 4 shows the key technology for fully dispersing the CNT. **Figs. 4(a)** and **(b)** are 2D-TEM and 3D-TEM images from a 100-nm-thick composite with 4.4% CNT. There are some areas without any CNT reinforcement that become weak areas. The weak areas are the reason why the effect is smaller in lower concentrations in **Fig. 3** and modulus of 2.7% becomes softer at high temperatures in **Fig. 2**.

Fig. 4(c) is a 2D-TEM image with 15.5% CNT. The fully dispersed CNTs make many cells and build a 3D-cell nanostructure to solve the critical dispersion issue in 2008 **[8 – 10]**. This process is named "cellulation".

Because the CNT is harder and stronger at high temperatures, the CNT nanostructure (cellulation) is sufficiently reinforced until high temperature is reached. Therefore the modulus of the cellulated composite (higher by 8.4% in **Fig. 2**) is stronger until 750°F (400°C). By same reason, the modulus of the cellulated composites in **Fig. 3** do not depend on the temperature between 397°F and 662°F (200° C and 350°C). This is the mechanism why the cellulated composite is stronger at high temperatures.

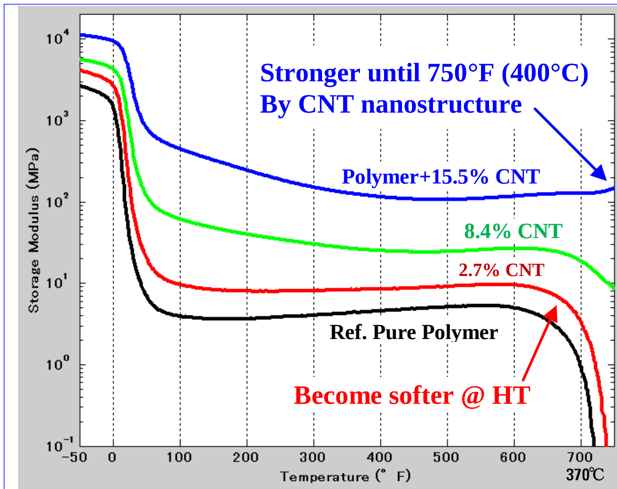

Fig. 2: Modulus vs. temperature of CNT-polymer composites.

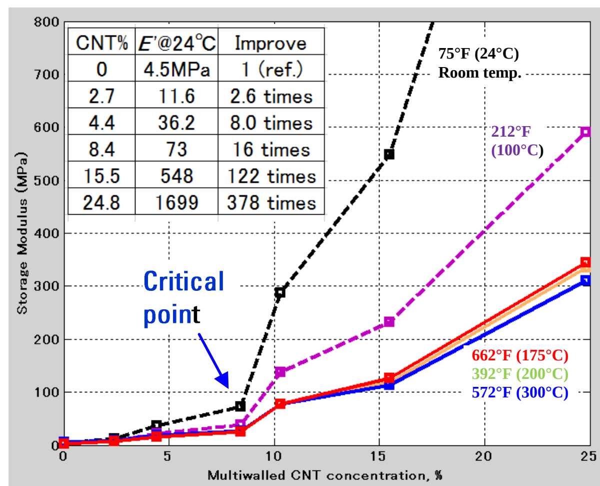

Fig. 3: Reinforced effect on CNT concentration.

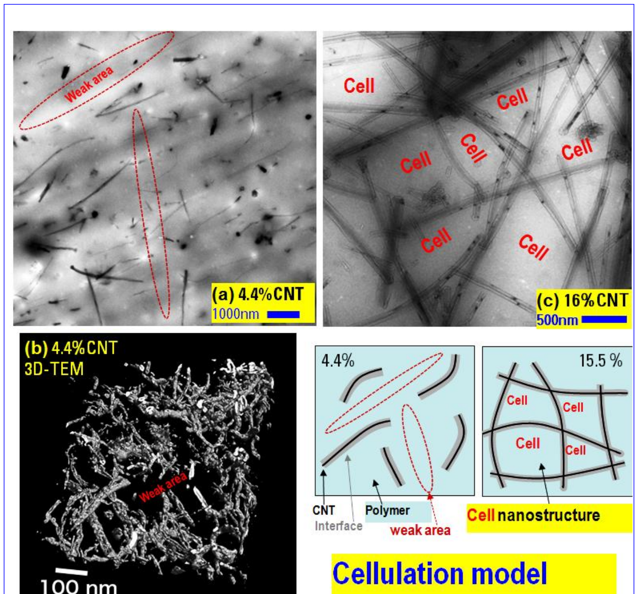

Fig. 4: Cellulation model, reinforced by CNT nanostructure.

3.2 Treatment Processes for Bonding

Poor bonding between CNT and soft matrix is another critical issue for CNT-polymer composites. We solved this problem in 2008 [8] by a specialized physical treatment process to optimize the surface roughness of the CNT. **Fig. 5(a)** is a TEM image of a standard MWNT with a fine surface. We used the standard MWNT to make a CNT-polymer composite which was submitted to the tensile test. **Fig. 5(b)** is an SEM image from the fracture surface produced by the tensile test. There are many CNT on the fracture surface because the CNT pulls off from the polymer due to poor bonding. **Fig. 5(c)** is another TEM image from same type MWNT but after a special treatment to optimize the surface condition. **Fig. 5(d)** is an SEM image from tensile fracture using the special CNT. All CNT are pulled before breaking by better bonding. The strength of the CNT used is 100% after the special treatment.

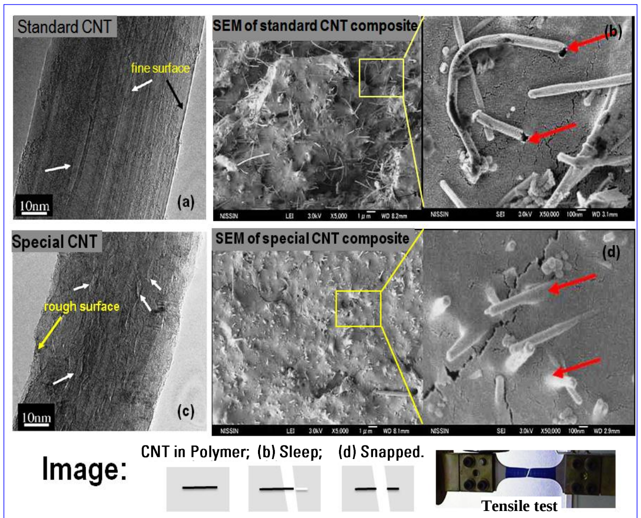

Fig. 5: Improved bonding between CNT and polymer from specialized treatment of the CNT surface.

3.3 Properties of the Developed Nanomaterial

By applying the new cellulation technology and treatment methods, we are able to develop a novel nanocomposite material with properties as listed in **Table 1**.

Sealing systems utilizing this material showed a good high-temperature performance while meeting good low-temperature performance. The reference materials listed in **Table 1** (Control 1: FKM-based standard material used in the oilfield and Control 2: FFKM-based for use at extreme high temperatures) are commercially available options. A comparison of tensile test results shows that the new nanocomposite material has comparable properties with the Control 1 and Control 2 options at lower temperatures while exceeding both at higher temperatures.

From aging results (heat resistance), the ***CS*** (compression set) performance of the new material exceeds both the Control 1 and Control 2 options. Compression set is an important parameter for sealing reliability, with a lower number better for performance.

The measured ***Tg*** (glass transition temperature) of the new material is the lowest of the three and indicates its suitability for good low-temperature performance.

Property	Temperature	Present Nano-material	Control 1 (Existing FKM)	Control 2 (Existing FFKM)
Ts, MPa	77°F (25°C)	15.8	11.9	15.0
Eb, %		100%	90%	90%
Ts, MPa	350°F (175°C)	8.4	4.3	–
Eb, %		60%	40%	–
Ts, MPa	500°F (260°C)	6.1	1.8	4.8
Eb, %		40%	10%	40%
CS, % 70hrs/Air	200°C	19%	28%	47%
	260°C	39%	–	83%
Tg, by DMTA		–11°C	–3°C	13°C
Min. Operation Temp		–10°C	–5°C	40°C

Table 1: Properties of the present material and reference materials measured following AS 2-223 O-rings using ASTM methods and real seal test in pressure/temperature. ***Ts***: Tensile strength, ***Eb***: Enlongation. ***CS***: compression set. ***Tg***: Glass transition temperature.

3.4 Performance Reliability and Field Tests

We have conducted extensive testing of the new nanomaterial to check its reliability and durability. Testing included chemical-resistance tests in hydrocarbon (oil), saltwater, H_2S, and CO_2 in HPHT conditions.

We also performed life testing in HPHT conditions to confirm the sealing reliability. **Fig. 6** shows the estimated life of the new sealing system to be 262 hours at 36,500 psi, 510°F (265°C) in a stable oil from laboratory testing.

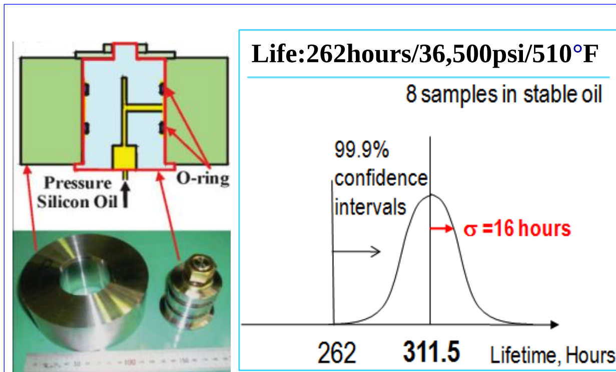

Fig. 6: HPHT sealing life test results.

Not only in high temperatures, but seal performance in low temperatures is important for deepwater and cold regions. **Fig. 7** presents results from testing O-ring sealing systems made of the new nanocomposites covering sealing capabilities in low temperatures. For deepwater operations, estimated sealing performance needs at a water depth of 5,000 meter is in the range of 15,000 to 20,000 psi under certain operating conditions. The minimum operation temperatures are show on the **Fig. 7** and in **Table 1**.

The FFKM does not meet deepwater operation requirements and can only seal about 6,000 psi at the low temperature range of 40°F (4°C: temperature in seabed, **Fig. 1**). These results clearly show the superior sealing capabilities of sealing systems with the new nanocomposite material.

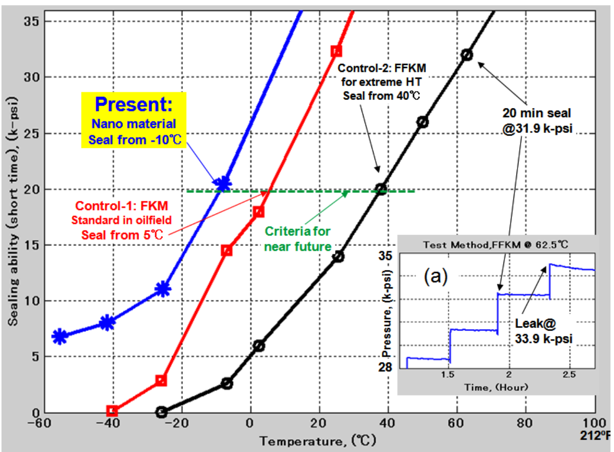

Fig. 7: Sealing ability in lower temperatures. Testing consisted of stabilizing the temperature of the HPHT setup at a select level and applying the pressure in steps each held for 20 minutes (a). Monitoring the pressure during the 20-minute holding time identifies the maximum sealing pressure. For example, the pressure steps uptil up to 31,900 psi at 145°F (62.5°C) are stable whilereas the pressure step at 33,900 psi is dropping with time. We used this data to estimate the maximum sealing pressure of Control 2 to be 31,900 psi.

After a series of laboratory tests, sealing systems based on the new nanocomposite material were tested extensively in the oilfield locations around the world. **Fig. 8** shows some of the locations where sealing systems based on the new nanocomposite material have been successfully tested.

4 CONCLUSIONS

We have demonstrated that the newly developed technologies for MWNT dispersion, cell structure creation, and bonding to base polymer are enabling us to create novel nanocomposite materials. The sealing systems based on one of the nanocomposites we have developed are shown to have superior sealing performance in both high- and low-temperature areas with successful field trials.

Fig. 8: Locations of successful field tests of sealing systems based on the new nanocomposite material.

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