Puncture-Healing Properties of Carbon Nanotube-Filled Ionomers

Final Report

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Puncture Reversal in Ethylene Ionomers – Mechanistic Studies

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Introduction

Ionomers are polymers that contain ionic groups in relatively low concentrations along the polymer backbone. These ionic groups, in the presence of oppositely charged ions, form aggregates that lead to novel physical properties of the polymer. React-A-Seal® and Surlyn® are poly(ethylene-co-methacrylic acid) (EMAA) ionomer-based materials and Nucrel® is the EMAA acid copolymer neutralized to produce Surlyn®. React-A-Seal®, Surlyn®, and Nucrel® recover into their original shapes following a high impact puncture at velocities ranging from 300 to 1200 ft/s ("self-healing"). This self-healing process may be of great benefit in space applications where structures are exposed to matter impacts. A thermal IR camera indicated a temperature increase to 98°C for Nucrel® 925, Surlyn® 8940, React-A-Seal®, and Surlyn® 8920 after initial penetration. To understand and generalize the observed phenomena, questions concerning the mechanism of the puncture resealing must be answered. One suggestion is that the elastic character of the melt created by the puncture drives the self-healing. This inference is based on the observed temperature rise of ~3°C above the melting temperature of the samples (~95°C) during the impact.

With the expectation of gaining additional insight into the self-healing phenomenon, a thermodynamic and viscoelastic investigation was conducted using primarily DSC and DMA. Surlyn® and React-A-Seal® showed the characteristic order-disorder transition at ~52°C that has been reported in literature. Master curves were constructed from the creep isotherms for the four EMAA samples. An aging study was performed to investigate the irreproducibility and "tailing effect" observed in the creep data. The aging study indicated that, with increased aging time and temperature, changes in the polyethylene matrix lead to complexities in morphology resulting in changes in the magnitude and shape of the creep curves.

As a result of the thermodynamic, viscoelastic, and high-speed impact experiments it has been theorized that self-healing can occur in Nucrel® 925, Surlyn®

8940, React-A-Seal®, and Surlyn® 8920 because of two features, ionic aggregation and complex flow behavior.

Results and Conclusions

The research in this study suggested that ionic aggregation and melt flow behavior are two characteristics that contribute to the self-healing ability of Nucrel® 925, Surlyn® 8940, React-A-Seal®, and Surlyn® 8920.

Nucrel® 925 (EMAA) exhibited weak aggregation, possibly due to intermolecular and intramolecular attraction of the polar carboxyl groups. Aggregation was inferred from the presence of an order-disorder transition measured in the DSC (Table 1). However, the order-disorder transition was not detected in the dynamic or viscoelastic experiments, hence the proposal of weak aggregation.

Sample	DSC T_i	T_i of α' peak at 10 Hz	Temperature of Slope Change in the Creep Data
Nucrel® 925	52.5°C	-	-
Surlyn® 8940	51.9°C	50.2°C	55°C
React-A-Seal®	52.2°C	50.3°C	55°C
Surlyn® 8920	52.6°C	59.3°C	58°C

Table 1. Comparison of the order-disorder transition temperatures from the DSC, DMA frequency dependent data, and the DMA creep data.

Surlyn® 8940 (EMAA-0.30Na), React-A-Seal® (based on EMAA-0.30Na), and Surlyn® 8920 (EMAA-0.60Na) displayed stronger aggregation due to increased ionic interactions with increased sodium neutralization. These EMAA ionomers exhibited an order-disorder transition in the DSC, the dynamic, and the viscoelastic experiments (Table 1).

The thermal IR images (Figure 1) captured during the high-speed bullet impact testing showed a uniform increase in the temperature of the EMAA samples to ~5°C above their melting temperatures (~95°C) following impact. The large temperature increase, 70°C above ambient temperature, caused by the impact suggested that melt flow properties were contributing to self-healing.

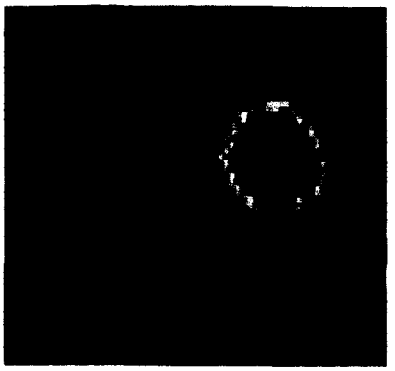

Figure 1. A thermal IR image from React-A-Seal®. The blue represents ambient temperature (~28°C). The dark pink (~98°C) represents the point of bullet penetration. The colors radiating out from the dark pink represent the dissipation of heat from the point of entry.

The melt flow properties were measured using a rheometer (Figure 2). Nucrel® 925, Surlyn® 8940, React-A-Seal®, and Surlyn® 8920 exhibited viscosities on the order of ~ 10^4 - 10^6 Pa-s at temperatures between 90°C to 150°C (Table 2). This increased viscosity, compared to polyethylene (~23 Pa-s), was speculated to be a direct result of aggregation, especially ionic aggregation.

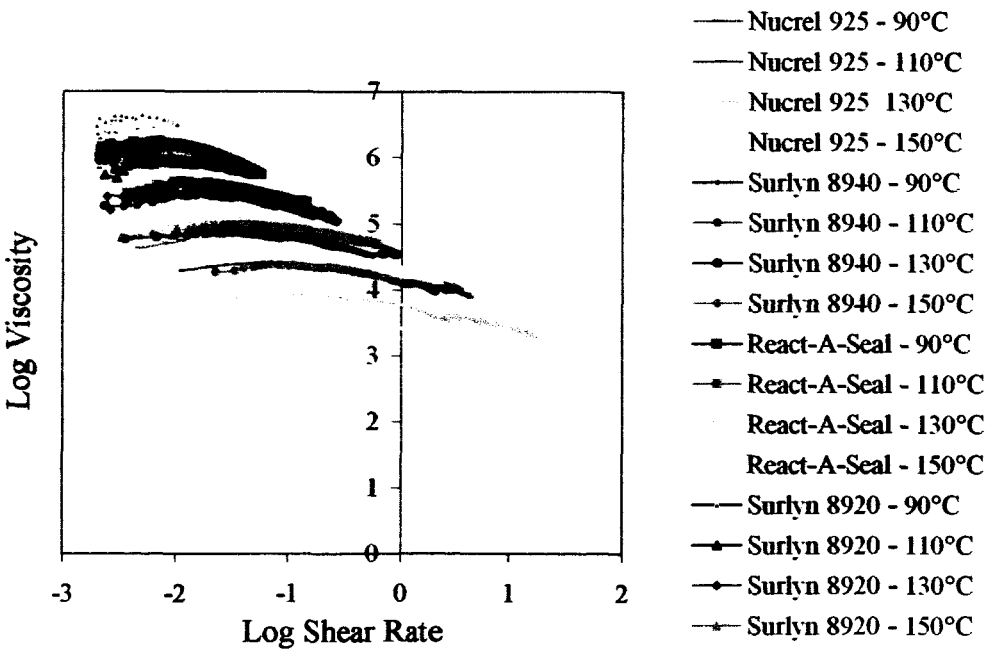

Figure 2. Graph of viscosity as a function of shear rate for Nucrel® 925, Surlyn® 8940, React-A-Seal®, and Surlyn® 8920 at 90, 110, 130, and 150°C.

	Temperatures Measured				
	90°C	110°C	130°C	150°C	units
Nucrel® 925	$3.8*10^4$	$8.5*10^3$	$2.1*10^3$	$5.6*10^2$	Pa-s
Surlyn® 8940	$8.5*10^5$	$1.6*10^5$	$3.6*10^4$	$9.7*10^3$	Pa-s
React-A-Seal®	$5.6*10^5$	$2.2*10^5$	$5.1*10^4$	$1.7*10^4$	Pa-s
Surlyn® 8920	$3.2*10^6$	$5.2*10^5$	$1.3*10^5$	$5.1*10^4$	Pa-s

Table 2. Apparent viscosities reached at the maximum stresses.

Together, the high viscosity and the resistance to motion of the aggregates raise the amount of energy absorbed by the EMAA samples upon high-speed impact. EMAA samples seem to self-heal if enough energy is transferred from the projectile to the sample to cause a temperature increase above the melting temperature. The increased elastic character of the melt, due to viscosity, primarily drives the healing phenomenon.

Future Work

Additional experiments are essential for continued clarification of the polymer and ionomer characteristics required for self-healing.

To better understand the unexpected healing of Nucrel® 925, other polymers, for example nitriles, amides, urethanes, and carbonates with stronger intermolecular and intramolecular forces could be studied under high-speed impact. The puncture reversibility or irreversibility of these materials would elucidate the importance of intermolecular and intramolecular aggregation.

The aged samples (annealed) could be shot under high-speed impact to learn more about the healing of the EMAA ionomers. This experiment would provide information on the effect of increased crystallinity on healing. Also, due to the disordered state of the ionomers during aging, if healing still occurred with high-speed impact, perhaps then ionic aggregation does not aid in healing. Testing of other ionomers with varying types and concentrations of cations could be performed if it is determined that aggregation is in fact necessary for healing.

It is also important to continue understanding how aggregation and flow behavior alter the thermal, physical, and mechanical behaviors of polymers and ionomers. A

threshold velocity could be observed for healing if a method were developed to vary the velocity of a projectile. This threshold velocity could then be converted into energy and possibly correlated to the amount of energy needed to overcome thermal and mechanical transitions as measured in the DSC or DMA.

In addition, to better understand the elastic melt flow behavior of these EMAA materials, the melt elasticity could be measured.

Finally, a high-speed camera that captures images at more than 10,000 frames per second could be used to visually observe the healing phenomenon. With this visual observation, perhaps the elastic behavior, due to the high viscosity of the ionomers or polymers could be investigated.