

## **Bonding Styrenic Copolymers and Thermoplastic Elastomers in the quest to replace PVC**

*Kyle Rhodes – Dymax Corporation*

*Nadine Blaesing – Dymax Corporation*

*Enercon Industries Corporation*

High performance polymers are often selected for applications that demand retention of structural and dimensional integrity under exposure to aggressive chemical and elevated temperature conditions. One such cost-effective performance polymer choice is plasticized PVC. However, significant attention has been placed on evaluating more environmentally and biologically-friendly polymers. Styrene-ethylenebutylene-styrene (SEBS) copolymer rubbers, SEBS/polypropylene blends, TPEs (thermoplastic elastomers) and polypropylenes are emerging as high performance alternatives. TPEs in particular are being employed to replace plasticized, low-durometer PVC in medical device applications, where biocompatibility characteristics are crucial. Adhesive bonding to these polymers, however, can be challenging.

### **PVC**

Commercially available PVC is highly branched and has low crystallinity. PVC with high molecular weight (K-Value > 100 with number average molecular weight up to 150,000) has a number of advantages, such as more ordered structure, more linearity, higher degrees of crystallinity and higher mechanical strength. PVC is plasticized with so called "monomeric" and low molecular weight "polymeric" plasticizers. Low molecular weight "polymeric" plasticizers are oligomeric polyester materials which are liquid at ambient temperatures.

Due to its excellent price-performance balance, plasticized PVC is widely used in many applications. In the medical industry, plasticized PVC is a dominant material used for the storage of IV fluids, dialysis solutions, blood bags connectors and tubing. This derives from PVC's clarity, strength, ability to withstand temperatures as low as -40°C and as high as +121°C, sterilization with steam, ETO and gamma radiation. The most preferred plasticizer for medical grade PVC is DEHP commonly known as DOP even though other plasticizers could be used for specialized applications. DEHP plasticized PVC containers have been used for the collection of blood and blood components for the last 45 years. DEHP has been shown to have very beneficial effects in maintaining the viability and long-term storage of RBCs. Other components in blood such as platelets have a higher metabolic rate and so containers for their storage must have higher permeability to oxygen and carbon dioxide. This is achieved by using other plasticizers such as trimellitates and citrates[1].

However, there are two primary drivers in the search for PVC alternatives. First, plasticized PVC has an undesired environmental impact related to the release of dioxins when incinerated in an uncontrolled manner [2]. Secondly is the concern that PVC plasticizers (so-called "oestrogen mimics") may migrate into the human body [3]. Potential alternatives for plasticized PVC tubes are polymer compositions containing polypropylene (PP) in combination with an elastomeric block copolymer. These compositions do not contain "oestrogen mimics" nor do they release dioxins when incinerated. Since the 1970s there has been active interest in developing kink resistant, flexible medical tubing based on styrene block copolymers (SBC's) [4].

SBCs are thermoplastic elastomers consisting of polystyrene (PS) endblocks chemically joined by a rubber midblock. The rubber midblock is most often composed of polybutadiene, polyisoprene or their hydrogenated poly-olefinic versions ethylene-butylene and ethylene-propylene. Since rubber and hard polystyrene blocks are incompatible, strong phase separation results in the formation of polystyrene domains. These domains act as physical crosslinks and can be broken and re-established by a combination of shear and temperature. The amount of shear required to process SBCs depends on the polystyrene mol weight (Mw) and type of rubber midblock. Styrene-Ethylene-Butylene-Styrene (SEBS) SBC's normally form stronger domains than their unhydrogenated predecessors.

A new family of hydrogenated SBC's appears to be closing the performance gap with plasticized PVC. This family is based on enhanced rubber segment (ERS) midblocks which contain a higher butylene content than the more traditional SEBS midblocks. The benefits of ERS-SEBS polymers include enhanced processability and improved

compatibility with polypropylene[5]. The fine network of the ERS-SEBS blend leads to a significant improvement of transparency. Another effect of the improved compatibility with PP is a broadening of the glass transition temperature ( $T_g$ ) below room temperature. The improved compatibility opens up an array of material properties making SBC-PP blends highly suitable for plasticized PVC replacement.

### **The Application**

Bonding to these new materials can be challenging due to the lack of bondable molecules along the polymer surface. Special considerations are necessary when evaluating new applications using these materials. One recent case study included a medical device OEM that was redesigning two tubing manifolds previously constructed of plasticized PVC. One new material to be utilized was GLS Versaflex CLE 85 TPE, a A-85 hardness TPE, which was to be bonded to itself. A 2<sup>nd</sup> part of the device had multiple ports, which required either a 50:50 blend or a 60:40 blend of SEBS/PP (K-Resin Kraton G1645M linear triblock copolymer/ Borealis SC820CF) extruded tubing, which was to be bonded to molded parts. These molded parts potentially could have used Lyondell Moplen RP340N Random Copolymer Polypropylene (RCP), Lexan 141R polycarbonate, or K-Resin KR03BR Styrene-Butadiene Copolymer (SBC). One light curable adhesive demonstrated high adhesion to all of the various components. An Enercon surface treatment system was used prior to bonding to improve adhesion and adhesion consistency.

### **Adhesive Selection**

Given the wide variety of adhesives available, selecting the right adhesive can seem daunting, yet it is just as crucial as selecting the right TPE and process treatment for the specific application. Medical-grade adhesives must provide reliable adhesion to chosen substrates, achieve the required bond strength, and provide a bonding in a fast, robust assembly process. The development of acrylated urethane adhesives which cure in seconds under exposure to UV and visible light (300-500 nm range) and the associated curing lamps which emit these wavelengths (up to intensities of 15 W/cm<sup>2</sup>) have been critical to the advancement of high-throughput medical device assembly lines. Light-curing enables assembly scenarios that range from manual assembly of tube sets and catheters to fully-automated, high-speed turn-key systems for the manufacture of needle components.

Adhesive selection requires a review of the assembly and bonding process envisioned by the engineer. Primary focal points include required throughput, substrates intended for bonding, and adhesive viscosity (which impacts dispensing, flow, and adhesive placement). Since the reliability of the medical device is of utmost importance, the ability to assure a high-quality adhesive bond is critical. Pre-cure and post-cure inspection of the bond line can be greatly enhanced by an ability of the adhesive to 1) fluoresce under a black light and 2) change color during the cure process. This improves the ease of inspection for adhesive presence, adhesive location, bond line uniformity, as well as verification that the adhesive has reached full cure. Early detection of less-than-complete cure and bond line leak pathways, air bubbles, or voids allows for more immediate process corrections.

### **Selecting the Curing Systems**

The selection of the curing system should be co-optimized with the selected adhesive(s), coating, or other light curable formulation. Curing systems range from low-power flood lamp systems (which emit a broad spectrum of wavelengths over an area) to medium and high-power flood lamp sources mounted on conveyor systems. By incorporating multiple light sources, three-dimensional curing systems are also available. Spot lamp sources are particularly useful in delivering a localized curing energy to smaller areas (<15 mm). Advancements in lamp technology and design have increased the available power output, and enabled the use of multi-pole lightguides that can provide up to four individual curing spots emanating from a single light source. This provides either optimum overlap of cure beams in a single adhesive bond line area, or an ability to cure in up to four individual adhesive locations. A recent advancement in lamp source has been the development of LED curing systems which can emit a discrete wavelength at various intensities. These units offer the advantage of high intensity while yielding a 50,000 hour LED life. A key benefit of LED curing derives from its "cool cure" characteristic. Thermally-sensitive polymer materials cured with LED lamps will generally not experience a high temperature rise, and thus will avoid warping on thin-walled catheters or tubing. LEDs are usually less efficient than broad spectrum lamps (which emit a wide range of wavelengths), so adjustments in the process may be required to reach full cure.

Advancements in adhesive chemistry development are helping to reduce the differential in cure times and bond characteristics between discrete wavelength LED lamps and broad spectrum bulb style lamps.

The primary key to selecting any lamp is to identify the minimum and maximum intensity and duration of exposure. The selection process for these criteria should take into account the tensile strength achieved, complete depth of cure, an adequate surface cure, as well as a safety margin to account for process variations.

Detailed within Table 1 below are the experimental parameters for evaluating the potential for TPE conversion:

| Materials/Process Employed         | Properties  |
|------------------------------------|---|
| <b>GLS Versaflex CLE 85</b>        | High clarity TPE  |
| Shore A Hardness                   | 85  |
| Specific Gravity                   | 0.9   |
| Tensile at Break (PSI/Mpa)         | 1500/10.3   |
| Elongation at Break (%)            | 600   |
| 300% Modulus (PSI/Mpa)             | 850/5.9   |
| Clarity (%)                        | <5  |
| Properties                         |   |
| <b>Dymax 1161-M</b>                | UV/visible light cure, blue fluorescing                 |
| Durometer Hardness                 | D70   |
| Viscosity, cP (20rpm)              | 300 (nominal)   |
| Tensile at Break (PSI/Mpa)         | 2300/16   |
| Elongation at Break (%)            | 68  |
| Modulus (PSI/Mpa)                  | 40,000/280  |
| Linear Shrinkage (%)               | 0.6   |
| Trial Parameters                   |   |
| <b>Enercon Dyne-A-Flame System</b> | 3-dimensional flame plasma surface treatment technology |
| Burner Technology                  | High velocity drilled port #24 series                   |
| Treatment Speeds                   | 100fpm, 200fpm  |
| Air/Gas Ratio                      | 10:1  |
| Treatment Gap                      | 2 inches  |
| Surface Tension Levels             | 60 mN/m, 46 mN/m  |

**Table 1. Experimental Parameters – Medical Application 1.**

**Application I**

Sample coupons of the GLS Versaflex CLE 85 (TPE), were flame-treated using an Enercon Dyne-A-Flame surface treatment system to compare adhesion outcomes at high surface tension levels and at low surface tension levels (untreated). It should be noted that preliminary trials using blown air plasma and gas-phase blown arc chemical plasma discharge treatments were not as successful in promoting optimal adhesion results as flame plasma technology. Coupons were sent to Dymax for the respective application of 1161-M light-



**Figure 1. Photo of Instron technique for peel strength**  
(Picture courtesy Instron)

curable adhesive and curing. Peel tests of the TPE substrate coupons bonded to each other with and without flame plasma treatment were subsequently conducted. Peel test results indicated that light curable adhesive 1161-M improves peel strengths when the TPE has been flame treated.

**Test Procedure:**

T-peel test at 2 in/min on an Instron 4467.

**Table 2. Test Procedure Results**

|           | Peel Strength [lbs/in] |
|-----------|------------------------|
| Untreated | 2                      |
| Treated   | 47                     |

**Table 3. Experimental Parameters – Medical Application II  
Materials/Process Employed - Substrates**

|                   |   |
|-------------------|---|
| <b>Tubing</b>     | Kraton G1645M/Borealis SC820CF 50/50 Blend            |
|                   | Kraton G1645M/Borealis SC820CF 60/40 Blend            |
| <b>Connectors</b> | Lyondell Moplen RP340N Random Copolymer Polypropylene |
|                   | Lexan 141R Polycarbonate                              |
|                   | K-Resin KR03BR  |

**Properties**

|                            |   |
|----------------------------|---|
| <b>Dymax 1161-M</b>        | UV/visible light cure, blue fluorescing |
| Durometer Hardness         | D70                                     |
| Viscosity, cP (20rpm)      | 300 (nominal)                           |
| Tensile at Break (PSI/Mpa) | 2300/16                                 |
| Elongation at Break (%)    | 68                                      |
| Modulus (PSI/Mpa)          | 40,000/280                              |
| Linear Shrinkage (%)       | 0.6                                     |

**Trial Parameters**

|                                    |   |
|------------------------------------|---|
| <b>Enercon Dyne-A-Flame System</b> | 3-dimensional flame plasma surface treatment technology |
| Burner Technology                  | High velocity drilled port #24 series                   |
| Treatment Speeds                   | 100fpm, 200fpm  |
| Air/Gas Ratio                      | 10:1  |
| Treatment Gap                      | 2 inches  |
| Surface Tension Levels             | 60 mN/m, 46 mN/m  |

Sample coupons of SEBS/PP blends made of Kraton G1645 (SEBS) and Borealis SC820CF (PP) were flame-treated using an Enercon Dyne-A-Flame surface treatment system to compare adhesion outcomes at both high surface tension levels and at low surface tension levels (untreated). It should be noted that preliminary trials using blown air plasma and gas-phase blown arc chemical plasma discharge treatments were not as successful in promoting optimal adhesion results as flame plasma technology. Coupons were then sent to Dymax for the respective application of 1161-M light-curable adhesive and curing. The SEBS/PP blends were bonded to the treated RP340N (RCPP), untreated Lexan 141R (PC) and K-Resin KR03BR to simulate typical tube to connector joints. Lap shear testing of samples with an overlap of 0.25 inches after flame plasma treatment and without treatment were subsequently conducted.

**Test Procedure:**

Shear strength testing at 20 in/min on an Instron 4467 Tensile Analyzer.

**Untreated**

|                      | PP      | PC      | K-Resin |
|----------------------|---------|---------|---------|
| <b>SEBS/PP 50/50</b> | 50 psi  | 187 psi | 185 psi |
| <b>SEBS/PP 60/40</b> | 117 psi | 168 psi | 170 psi |

**Treated**

|                      | PP      | PC      | K-Resin |
|----------------------|---------|---------|---------|
| <b>SEBS/PP 50/50</b> | 284 psi | 244 psi | 290 psi |
| <b>SEBS/PP 60/40</b> | 193 psi | 226 psi | 285 psi |

**Conclusion**

High-clarity TPE flame-treated using high-velocity drilled port technology at a specific port velocity (flame power) and adhered by a Dymax light-curable adhesive 1161-M improved T-Peel force of the adhesive by a minimum of 2200%. Similarly, SEBS/RCP blends were flame-treated using high-velocity drilled port technology and adhered by a Dymax light-curable adhesive 1161-M improved shear strength significantly. Interestingly, the SEBS/PP 50/50 blend showed a 468% increase in shear strength using PP in the blend with flame treatment vs. 30% increase using PC and a 57% increase using the K-Resin, respectively. Yet, the K-Resin blend netted the highest overall shear strength at 290 psi. It would appear that applying specific flame treatment protocols to hydrogenated SBC's seems to offer the potential of competitive adhesion performance relative to plasticized PVC.

Replacements for plasticized PVC can be found by evaluating both TPE thermoplastic elastomers and SEBS/RCP blends (Styrene-ethylenebutylene-styrene/polypropylene), and achieve good adhesion through the selection of the right adhesive and surface treatment system.

**References**

- [1] "Alternatives for PVC in Medical Applications, Though Developed, Are Less Cost Effective", Smarttech Global Solutions Ltd., 2003.
- [2] Kalisvaart, M.G., Wright, K.J., "Novel Styrenic Block Copolymers for Medical Tubing", American Chemical Society Proceedings, 2009
- [3] Dorey, C.N., "Chemical Legacy – Contamination of the Child", Greenpeace, London, UK 2003, p.38.
- [4] Faselow, D.L. et al, "Flexible, Chlorine-free Multilayer Tubing, U.S. Patent 5,526,627, 1996.
- [5] "Kraton Polymers, Flexible Approach", The Manufacturer US, SayOneMedia Ltd., London, UK, 2008.