New tackifiers provide improved performance

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Executive summary

Ongoing development efforts for new, higher performing tackifiers have resulted in some novel research in this area. Results for one class of new materials are presented that show performance that is equal to or better than that of the current high grade and super tackifiers in natural rubber-polybutadiene rubber blends.

Tack measurements were performed in both high and low natural rubber content blends at one, three and eight days. Measurements also were made under standard and hot/wet conditions to better simulate performance in real world conditions. One of these new materials shows performance rivaling the current butylphenol- based super tackifier, but with an octylphenol resin. This represents truly unique performance for octylphenol-based resins.

TECHNICAL NOTEBOOK

Edited by Harold Herzlick

The use of tackifiers in rubber processing has been a common practice for decades. Tack has been defined numerous times, but perhaps the simplest definition is the ability of two materials to resist separation after bringing their surfaces into contact for a short time under a light pressure.¹

Tack is very important in the tire manufacturing process and other industries where multiple layers must be plied together and remain in place until curing is achieved. In addition, the adhesion of the layers is important during curing to prevent voids and bubbles from occurring and producing defects in the finished goods.

Originally coumarone-indene resins were used with natural rubber, but the advent of synthetic rubber and blends led to the need for a different class of more effective tackifiers. Phenolic tackifiers were the solution and have been in use for more than 40 years now in a wide variety of applications. In addition to the ability to impart tack to a wide variety of rubbers and rubber blends, they also can impart creep resistance during the inplant processing of uncured articles.

Phenolic tackifiers to date have been of two main classes defined by the starting alkylphenol used to produce them. Most are based on the acid-catalyzed condensation of an alkylphenol and formaldehyde to produce a novolak resin.

The biggest class (by volume) is the materials based on p-tert-octylphenol (PTOP), resins, which are the mainstays of the rubber industry. A smaller, specialty group of resins is based on p-tertbutilphenol (PTBP) and includes not only phenol-formaldehyde resins but also phenol- acetylene resins. These latter resins have unique properties and commonly are referred to as “super tackifiers” because of their performance characteristics.
There have been many investigations into the mechanism of tackification. One of the most comprehensive is by Hamed who defined the observed tack in a compound by the term “relative tack” as the ratio of observed tack to the green strength of a material. Thus a perfect tackifier would have a relative tack of one, as the maximum tack is controlled by the green strength of a compound.

The factors that control the observed tack include the green strength of the material, the interdiffusivity of the two surfaces and the surface roughness. Others have explored the factors that control tack in a number of different rubber stocks and types of blends and the factors that affect the measurement of tack. For phenolic tackifiers in particular, there have been studies on their surface activity and computations on their structure and interactions in blends.

<table>
<thead>
<tr>
<th>Material</th>
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<tr>
<td>Natural Rubber</td>
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<tr>
<td>High-cis Polybutadiene</td>
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<td>Carbon Black</td>
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<td>Resin</td>
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Fig. 1. Cure profile measurements in 75/25 blends.

Fig. 2. Cure profile measurements in 25/75 blends.

Fig. 3. Standard tack measurements in 75/25 blends.

Fig. 4. Standard tack measurements in 25/75.
Experimental

**Tackifier resins**

Standard grade PTOP- and PTBP-based tackifiers were commercial Schenectady International Inc. products. Commercial super tackifier was a sample of Koresin from BASF. The new tackifier resins were either prepared in the laboratory, pilot plant or factory depending on grade. A laboratory preparation is included below as an example.

**Copolymer synthesis**

The appropriate alkylphenol and an acid catalyst were loaded in a flask and mixed while heating the flask to 90°C. Formaldehyde (50 percent aqueous solution) then was added slowly to the flask while keeping the temperature in the range of 90-100°C. After the addition was completed the temperature was raised to 135°C to complete the reaction. After completion of the ensuing reaction, the appropriate amount of a vinyl monomer was introduced to the flask and allowed to react with the novolak resin.

The water and byproducts in the mixture were distilled off first at 170°C and atmospheric pressure and then at 180°C at 74 torr. The resin was poured out and allowed to solidify in a pan. All resins then were pulverized and used in ground form. Final properties for Elaztobond T6000: ball and ring softening point (melt point) – 115-125°C, melt viscosity 2000 cP (175°C). Final properties for Elaztobond T2000: ball and ring softening point (melt point) – 120-130°C, melt viscosity 10,000 cP (175°C).

**Compound mixing**

All compound mixing was performed by Smithers Scientific Services Inc. in Akron according to ASTM D3182-89(2001). Compounds were mixed in a Farrel BR size Banbury mixer at a 65-percent fill factor to the total mixer volume.

**Physical property testing**

All physical property testing was performed by Smithers Scientific Services. An Oscillating Die Rheometer (ODR) was used to determine extent of cure and cure kinetics according to ASTM D 2084-01.

Original and aged physical property measurements were carried out following ASTM D412-98a(2002)e1. Hardness measurements (Shore A) were performed following ASTM D2240-03. Tear Resistance of Rubber measurements followed ASTM D624-00e1. Tack measurements were made using a B.F. Goodrich Portable Universal Tack Tester. Samples were stored under controlled conditions of temperature and relative humidity for up to eight days.
Results and discussion

The properties of natural rubber (NR)-polybutadiene rubber (PBdR) blends was measured over a range compositions from 75/25 to 25/75 (NR/PBdR). The tackifiers studied included a standard PTOP-based resin (SP-1068), a new PTOP-based copolymer (Elaztobond T6000), a standard PTBP-based resin (SMD 31144), a new PTBP-based copolymer (Elaztobond T2000) and a PTBP-based super tackifier (Koresin from BASF). A representative formula is shown in Table I.

Cure properties

We measured the cure profile of compositions containing each of the tackifiers at a 4 phr loading via oscillating disk rheometry. Two parameters are reported; ts1 as a measurement of relative scorch behavior and tc90 as guide to the total cure rate. The ODR results for the 75/25 compositions are shown in Fig. 1. It is instructive to compare results within an alkylphenol type first.

Comparing PTOP-based resins, the copolymer T6000 material gives a significant improvement in ts1 (2.80 min) over the standard material (SP-1068, 2.36 min.) This delay in cure initiation is reflected in a longer total cure time (tc90) for the T6000 material in exactly the same ratio (1.2), indicating the entire cure profile is the same, but delayed.

Making the same comparison for the PTBP resins shows the standard resin (31144) with the best scorch behavior of all three, with the copolymer and the super tackifier equivalent to each other. The total cure time for each of the PTBP resins is the same within experimental error. The other generalization to make is that PTBP tackifiers are scorchier than PTOP-based ones in high NR blends.

In high PBdR compositions, shown in Fig. 2, the results are somewhat different. Once again, there is a significant improvement in scorch behavior among the PTOP tackifiers copolymer to standard material. However, in this blend there is little difference in total cure time, which suggests that the rate of cure is higher with T6000 compared to the standard material.

In the PTBP family of tackifiers, the copolymer is now less scorchy than the standard material. However, their total cure times are exactly the same. The super tackifier is significantly less scorchy than the other PTBP resins in this composition. Its total cure time also is much longer, even more than the difference in scorch times when compared to the PTBP resins, suggesting it has a slower rate of cure. In this composition the only significant generalization that can be made is that the super tackifier will have a slower cure profile, both on initiation and total cure time.

Standard tack properties

Tack was measured under two different sets of sample storage conditions. The first was under “normal” conditions of 25°C and 50 percent relative humidity. Measurements were made on at least five samples for each composition. Samples were tested after one, three and eight days of storage on the exposed surface of each sample.

In high natural blends, shown in Fig. 3, there is a very wide range of tack results observed. In general, high natural blends have very good tack, but some of the comparisons are striking. There is a fivefold improvement in tack with the PTOP copolymer compared to the standard resin. In fact, the copolymer gives better tack performance than the PTBP super tackifier, a very unusual result. PTBP tackifiers historically outperform PTOP-based resins—compare 31144 to SP-1068, which gives about five times the tack of 1068. For the PTBP-based resins, the copolymer gives somewhat better performance overall when compared to the standard material. Its tack performance is also an improvement over that of the super tackifier.

Results for the 25/75 (NR/PBdR) compositions are shown in Fig. 4, and generally are fairly low as expected for low NR blends. Starting again with the PTOP tackifiers, the tack performance of the copolymer is about six times better than the standard material. In fact, the tack performance is roughly equivalent to the PTBP-based super tackifier. Comparing the PTBP tackifiers, the copolymer tack is improved by 25 percent over the standard resin. It gives equivalent initial tack to the super tackifier, but is somewhat lower over time.
This significant change with time for tackifiers is of some interest, and has not been reported on to our knowledge. Though our experiments to explain the phenomenon are ongoing, the observations here are worth pointing out. The PTBP-based super tackifier shows a significant improvement (ca. 1/3) from one to three or more days. Conversely, the PTOP-based copolymer compositions show a similar magnitude yet opposite change on storage.

**Hot and humid tack properties**

A similar protocol for testing hot and humid tack was employed, though measurements were made after one and seven days. The same number of samples was tested for each composition in the same way, only the storage conditions were changed to 40°C and 95-percent relative humidity.

For high natural rubber blends, the results are shown in Fig. 5 and mirror the standard measurements in that there is a wide range in performance but on the whole the tack is quite high. Once again, the PTOP copolymer far outperforms the standard resin. It even outperforms the super tackifier by more than threefold. Under these conditions, the PTBP-based novolaks give equivalent performance to each other. Both are about twice as effective as the super tackifier in hot and humid conditions for high natural blends.

In low natural rubber blends, the results (shown in Fig. 6) are much lower, just as they were in standard conditions. For PTOP materials, the relative results are similar. The copolymer material is once again about five times more effective than the standard resin.

It is also equivalent or better than any of the PTBP-based resins, including the super tackifier. All of the PTBP-based materials give essentially equivalent results and are all much more effective than the standard PTOP resin. Interestingly, the change in tack with time observed earlier under normal aging conditions is not readily apparent under hot and humid storage. The PTOP copolymer does show a significant improvement, but not in a systematic way based on base resin composition as seen earlier in this blend.

**Conclusions**

The cure and tack properties of a new class of tackifiers has been described and shown to be superior to existing homopolymer materials in natural rubber polybutadiene blends. Though the specific properties are dependent on the amount of natural rubber in the blend, in general copolymerization with a vinyl comonomer has several beneficial effects.

For PTOP-based resins the scorch behavior is improved significantly, independent of NR content. The total cure time is dependent on blend composition, with high NR blends exhibiting just a delayed cure profile, while in low NR blends the total cure time is unchanged. This suggests a change in rate of curing after a beneficial delay in initiation. Tack performance of the copolymer material under normal storage conditions is dramatically better than standard PTOP-based tackifier, to the point that it is equivalent to PTBP-based tackifiers and even super tackifiers. In hot and humid storage conditions the tack performance is unequalled.

**References**

Custom Mixing


The author

Timothy E. Banach received his doctorate from the University of Rochester in 1989 in mechanistic organic chemistry. He spent 10 years as a research chemist at General Electric Co.’s Corporate Research and Development Laboratory before moving to Schenectady International Inc.

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Presented at the ACS Rubber Division’s 168th Fall Technical Meeting, held Nov. 1-3 in Pittsburgh.