Rubber Science, **26**(1): 148-157, 2013

SUPERIOR TACKIFYING RESIN

Raj B. Durairaj

Research and Development Department

TWC Group/Techno WaxChem Pvt. Ltd, Kolkata – 700046, India

Received : 09 April 2013 Accepted : 10 May 2013

Raj, B.D. (2013). Superior tachifying resin. *Rubber Science*, **26**(1): 148-157.

Tackifiers or tackifying resins are used in the rubber compounds to provide tack during the building process of green tyres until they are vulcanized. Phenolic novolak resins based on *P-tertoctylphenol* (PTOP) and *P-tertbutylphenol* (PTBP) are predominantly used by the tyre industry due to their prolonged retention of tackiness. In the construction of radial and bias/belted passenger tyres, blends of styrene butadiene (SBR) and polybutadiene (BR) rubbers are generally used in the tread cap, under tread and side wall compounds. Due to relatively poor tack properties associated with BR and SBR compounds, high performance phenolic tackifiers are needed in the formulations of these rubbers. In addition, rubber compounds near the belt area of radial tyres should have high building tack even though they are predominantly natural rubber based compounds.

Super tackifier resin, called Koresin® (BASF Germany) is an alkylphenolic resin which provides prolonged tackiness in compounds containing synthetic rubbers. Koresin® is made from the reaction of PTBP with acetylene. Now, a new version of Koresin® was synthesized from the reaction of PTBP with acetaldehyde. This modified PTBP – acetaldehyde resin is called Technic KR-140. A comparison of performance and properties of Koresin® with Technic KR-140 in rubber compounds are presented in this paper.

Keywords: Building application, Koresin®, *p-tert*-butylphenol, Technic KR-140

INTRODUCTION

Modern radial and bias/belted passenger car, truck and bus tyres are designed to provide good crack and abrasion resistance, low hysteresis, low rolling resistance, and good mileage and service life. In order to achieve the above properties, tyre industries employ blends of natural rubber and synthetic rubbers, such as styrene butadiene (SBR) and polybutadiene (BR) rubbers in the rubber formulations, particularly in tread cap and under tread compounds. Natural rubber has sufficient inherent tack for most building applications so that tackifying agents may not be necessary. Styrene butadiene (SBR) and polybutadiene (BR) rubbers are nonpalar compared to other synthetic rubbers. Unlike natural rubber, SBR and BR do not develop surface peroxidal activity upon mastication. Therefore, SBR and BR rubber compounds have relatively poor inherent or processed tack properties.

Tyres are typically constructed by building layers of rubber-coated fabric one over another, followed by a breaker strip, cushion, and tread rubber compounds. These layers must possess sufficient surface tack to

Correspondence: Raj B. Durairaj (Email: raj.durairaj@technowaxchem.com)

maintain the desired relative position of the various parts prior to vulcanization. The term "tack" refers to the ability of two uncured rubber materials to resist separation after bringing them into contact for a short time under relatively light pressure (Hamed, 1981). Building tack of rubber compounds is an important pre-requisite to enable tyre building in flat blankets. Another important feature is retention of tack during storage of tyre segments. Tyre segments are pre-manufactured and then stored.

In rubber formulations, tackifier materials (generally resins) are often used to provide building tack to rubber compounds. Tackifiers, used in the manufacture of tyres, should be compatible with synthetic rubbers and exhibit the required tackifying effects. As tackifiers have a very little affinity with the synthetic rubbers there is no substantial reaction occurs between the synthetic rubbers and the tackifiers during processing and upon heating.

Tackifying resins can be divided into three groups: hydrocarbon resins, rosin resins and phenolic resins. Generally, there are two different types of tackifier resins used by the rubber industry: hydrocarbon and phenolic. Sometimes, blends of hydrocarbon and phenolic resin tackifiers are used. Hydrocarbon tackifiers provide good initial tack, but typically do not provide good long-term tack. Phenolic tackifiers provide good initial and long-term tack properties (Gwin *et al*., 1977; Magnus *et al*., 1991).

In the case of phenolic resin tackifiers, alkylphenolic resins based on *p-tert*-octylphenol (PTOP) and *p-tert*-butylphenol (PTBP) are predominantly used by the tyre and rubber industries. These alkylphenol novolak resins may be obtained by reacting alkylphenols such as *p-tert*-butylphenol (PTBP) or *p-tert*-octylphenol (PTOP) with aldehydes in the presence of acid catalysts (Fig. 1).

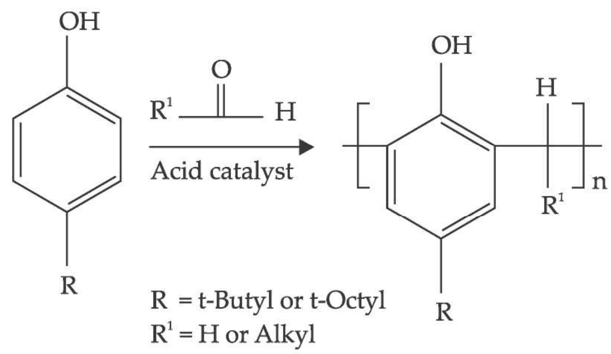

Fig. 1. Preparation of alkylphenols novolak resins

The polymerization of alkylphenols with aldehydes to prepare alkylphenolic novolak resins is well known (British Patent, 1967; Schmidt *et al*.,1981; Galkiewicz *et al*.. 1978; Banach *et al*., 2006). *P*-alkylphenol - aldehyde resins are linear low molecular weight products and are thermoplastic in nature. The novolaks produced from alkylphenols are more compatible with hydrophobic rubbers.

Normally, the tack performance of these alkylphenolic novolak resins depends on their molecular structure and molecular weights. In general, based upon the extensive use and tack performance data, the novolak resin obtained from *p-tert*-octylphenol and formaldehyde reaction is considered as a "general purpose" tackifying resin. Similarly, the resin obtained from the reaction of *p-tert*-butylphenol and formaldehyde is believed to be a "high performance" tackifying resin. But, the highest performance tackifying resin was obtained from the reaction of *p-tert*-butylphenol and acetylene with the following chemical structure.

The *p-tert*-butylphenol based on acetylene resin, known as Koresin®, was developed during the World War II in Germany as a tackifier resin for synthetic rubbers (Zoss *et al.*, 1949; Groote, 1951). This resin was found to be the most effective tackifier for polybutadiene (BR) and styrene-butadiene (SBR) rubbers and superior to alkylphenol-formaldehyde resin. Due to superior performance, Koresin® is often called the "Super Tackifier Resin".

Koresin® imparts the following properties to synthetic rubbers (Koresin®, 2006).

- Very high initial and extremely long-term tackiness
- No adverse effect on the rubber compound cure and scorch
- No interference on rubber to metal or rubber to synthetic fibre and fabric bonding
- Physical properties of the cured rubbers remain unchanged
- No effect on the performance of aged rubber compound properties
- Improves rubber compound process reliability
- Show extremely good performance in silica/SSBR based rubber compounds

Though Koresin® was developed about 70 years back; BASF is the only commercial scale of manufacturer this resin for tyre and other applications. Koresin® resin could also be synthesized from PTBP and acetaldehyde in the presence of acid catalysts (Groote, 1950; 1960; Groote *et al*., 1952; Marvel *et al*., 1949). The synthesis of this resin could be made using the following reaction scheme (Fig. 2).

The resin developed using PTBP and acetaldehyde were tested in the rubber compounds containing SBR and BR, and found to improve the building tack properties of tyre carcass and tread

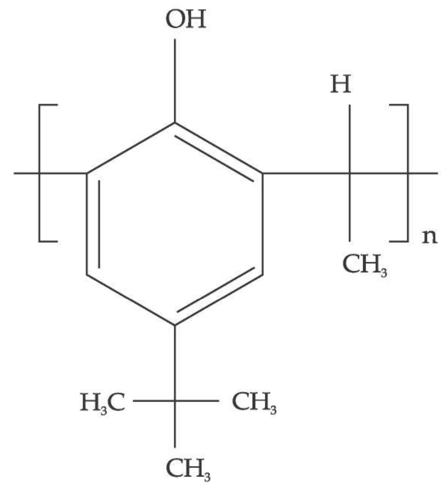

Fig. 2. Structure of tackifying resin obtained from *p-tert*-butylphenol and acetylene

compounds (Marvel *et al*., 1949; Howland *et al*., 194; Vredenburgh *et al*., 1972).

In the past, numerous attempts were made to duplicate Koresin®. Currently a modified resin was synthesized from the reaction of PTBP with acetaldehyde which showed structure similar to Koresin®. This modified PTBP – acetaldehyde resin is called Technic KR-140. Details of the Technic KR-140 resin against Koresin® are presented in this paper.

Experimental details and testing methods

A modified resin (Technic KR-140) was synthesized from PTBP with acetaldehyde using a proprietary procedure developed at R & D Department, Techno Wax Chem Pvt. Ltd., Kolkota.

FTIR spectra were recorded using a Bruker instrument. The performance of Technic KR-140 against Koresin® resin was evaluated using a rubber compound formulation outlined in Table 1.

Mixing of the rubber compound was done using a laboratory model Banbury (two-wing rotor mixer) of 1.5 L capacity.

Table 1. **Rubber compounds used in performance testing**

Rubber composition	phr
Natural rubber	30
Butadiene rubber	70
Carbon black (N 375)	80
Oil	4
Stearic acid	2
Zinc oxide	3
Insoluble sulphur	1
Tackifying resin	4
NS[a]	2.2
TMQ [b]	1.5
PPD[c]	1.6

a N-tert-butyl-2-benzothiazyl sulphenamide
b 2,2,4-trimethyl-1,2-dihydroquinoline
c N-(13-dimethylbutyl)-N^1-Phenyl-*p*-phenylenediamine

Rheometric properties were determined at 160 °C for 30 minutes using a moving die Rheometer according to ASTM D5289 method. The Mooney viscosity and Mooney scorch properties were determined in a Mooney viscometer (MV 2000 E) according to ASTM D 1646 method.

The green rubber compounds were cured in an electrically heated hydraulic press. The tensile and tear properties of cured compounds were measured using a Zwick UTM 1445 instrument according ASTM D 412 and ASTM D 624. The Shore A hardness was measured in a hardness tester according to ASTM D 2240 method.

Hysteresis was determined by measuring the tan δ properties of rubber compounds using a dynamic mechanical analyzer (DMA) at 10 Hz with 0.25 per cent strain.

Tack property measurements were measured using the Monsanto Tel-Tak instrument method (Beatty, 1969).

RESULTS AND DISCUSSION

Role of alkylphenolic tackifying resins in rubber compounds

Natural rubber can undergo oxidation in the presence of air or atmospheric oxygen and may produce hydroxyl or hydroperoxide groups at the surface of polymer chains. With natural rubber based compounds, the tack properties of milled or partially oxidized natural rubber can be attributed to the hydroxyl groups attached to the hydrocarbon chain of rubber molecules.

But, with synthetic rubbers, such as the butadiene (BR) and styrene-butadiene (SBR) rubbers, the absence of inherent tack may partly due to their lower reactivity towards atmospheric oxygen. Therefore, high performance alkylphenolic tackifying resins are used in the formulations containing BR and SBR. Alkylphenolic resins, compared to BR and SBR rubbers, are highly polar molecules in nature. When these polar alkylphenolic resins are mixed in non-polar rubbers, these ploar substances tend to move towards the surface of the compound. The action of polar groups at the surface of the rubber compound bring the surfaces together (Busse, 1946).

The tackifying action of alkylphenol – aldehyde resins may be pictured as crumpled rigid chains of *p*-alkylphenol residues joined by either methylene or substituted methylene bridges with hydroxyl groups appear at regular intervals on one side of the resin molecule. A pictorial view of tack imparted by the *p-tert*-butylphenol based tackifying resin in SBR or BR rubbers is shown in Fig. 3.

The tackifying action of *p*-alkylphenolic tackifying resins depends on the molecular weight of the materials. Tack properties are

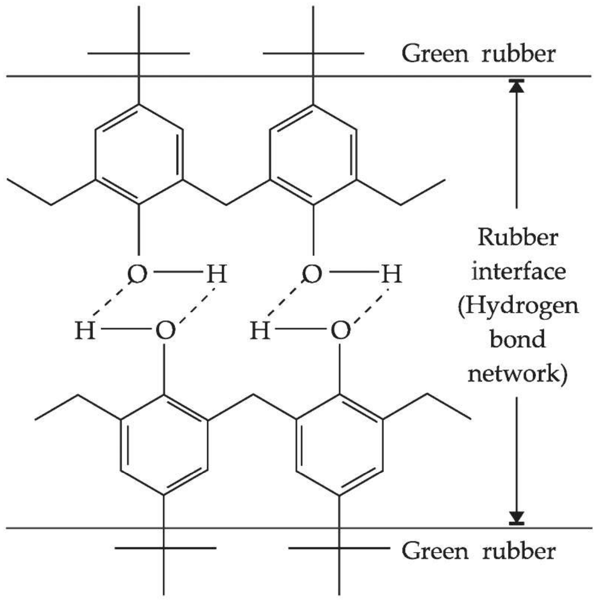

Fig. 3. Formation of hydrogen bonds from the *p-tert*-butylphenol hydroxyl groups present at the surface of rubber compounds

observed to increase when the molecular weights of resin increases. When the softening points of resins increase, the tack properties also increase, since the molecular weights are directly related to the softening point of the resin. This might be due to large number of hydrogen bonded chains present in the higher molecular weight resins (large number of *p*-alkylphenol residues). On the other hand, if the resin molecule is composed of two or three repeated *p*-alkylphenol residue then the resin loses much of its tackifying power. Therefore, to achieve the maximum tackifying effect in synthetic rubber compounds, alkylphenolic resins having high molecular weights are generally employed.

Tack properties of PTBP – Acetylene resins

In order to determine the effectiveness of PTBP-acetylene resins (Koresin®) in the synthetic rubber compounds, resins having different softening points or molecular weights were synthesized and evaluated (Zoss *et al.*, 1949). The tack data obtained from this study is summarized in Table 2.

From Table 2, it was evident that the tack performance of Koresin® type product primarily depended upon the molecular weight of resin. Higher softening point resin (higher molecular weight) exhibited higher tack in the synthetic rubber.

Tack properties of PTBP – Acetaldehyde resins

The PTBP-acetaldehyde resins were prepared and studied for their structural and tack performance characteristics with Koresin® (Marvel *et al.*, 1949). Table 3 shows the details of the effect of molecular weights of PTBP-acetaldehyde resins on the tack properties in synthetic rubber like SBR.

Table 2. **Tack properties of PTBP – Acetylene resins**

Resin	Softening point (^{0}C)	Tackifier rating (After 24 h)
PTBP Acetylene	155	16
	145	14
	130	13

Table 3. **Effects of molecular weight on the tack properties of PTBP-Acetaldehyde resins**

Softening point (^{0}C)	Molecular weight	Tackifier rating
75-78	460-469	4
90-95	494-540	8
110-115	770-778	9
119-123	844-866	9
Koresin®		
130-135	1046-1297	10
Technic KR - 140		
140-145	Approx.>1400	Approx. 10

Table 4. **Comparison of properties of Koresin® and Technic KR-140**

Resin	Koresin®	Technic KR -140
Physical form and colour	Yellow to brown pellets	Brown pastille
Softening point (^{0}C)	135-150	140 ±5
Density g/cm^3	1.02 – 1.04	1.02 – 10.05
Weight loss (70 ^{0}C/2 h)	0.019	0.009
pH (Aqueous alcohol solution)	4.0 – 6.0	4.0 – 6.0
Free monomer (HPLC, wt %)	2.2	2.0 – 2.3
Ash content (750 ^{0}C/h)	0.63	0.87
Solubility in hydrocarbons	Soluble	Soluble

From Table 3, it is clearly evident that the tack properties of PTBP – acetaldehyde resins also directly related to their molecular weights. Since the higher molecular weight products are expected to produce more inter-molecular hydrogen bonds at the interface of rubber layers, higher tack properties were observed with these resins.

Technic KR-140 resin

Technic KR-140 was prepared and its physical properties are summarized in Table 4 along with Koresin®.

As can be seen from Table 4, Technic KR-140 resin has softening point similar to Koresin®. The objective was to develop a

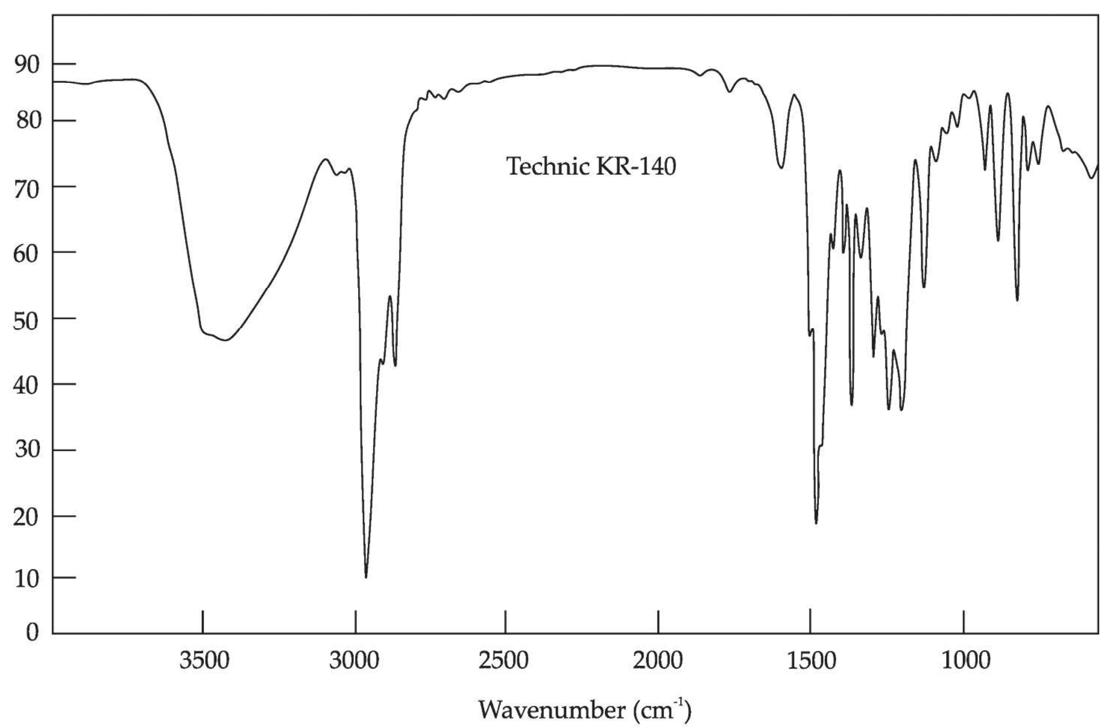

Fig. 4. FTIR spectrum of Technic KR-140 resin

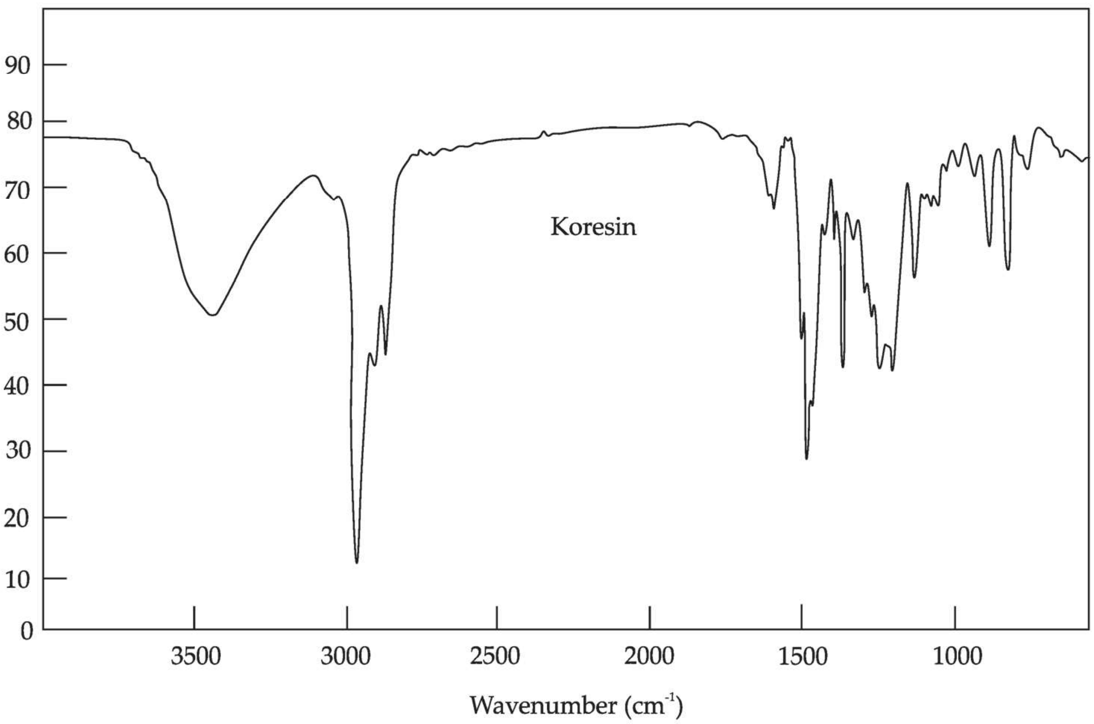

Fig. 5. FTIR spectrum of Koresin®

resin in the range of 140 – 145 °C softening point, which is very close to the softening point of Koresin®.

FTIR Spectra of Technic KR-140 and Koresin®

The FTIR spectra of both resins are given in Figs. 4 and 4.

From the FTIR data, Technic KR-140 resin showed good structural correlation (greater than 98 per cent) to Koresin® and is evident that Technic KR-140 resin is structurally similar to Koresin®.

Cure, Mooney viscosity and scorch properties

The Rheometer cure, Mooney viscosity and scorch properties were studied according to ASTM procedures. The data obtained are presented in Table 5 and Fig. 6.

Based on the Table 5 and Fig. 6 the Rheometer cure, Mooney viscosity (ML1+4), Mooney scorch and resilience properties of Technic KR-140 resin incorporated rubber are equivalent to that of Technic KR -140.

Tensile properties

The before and after aged tensile properties and hardness of rubber compounds are shown in Table 6.

Table 5. **Comparison of cure properties**

Property	Koresin®	Technic KR-140
Tmax, Lb.In	20.75	21.07
Tmin, Lb.In	2.98	3.05
Ts1, min	2.08	1.99
Ts2, min	2.53	2.43
T50, min	3.41	3.31
T90, min	4.96	4.88

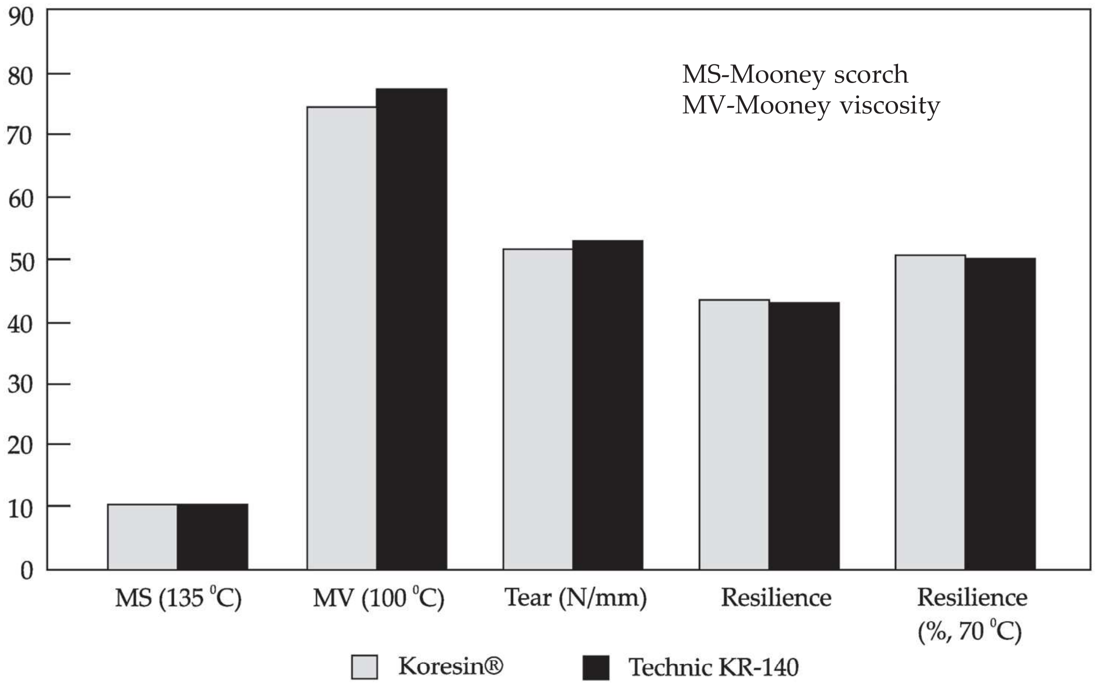

Fig. 6. Technological properties of the vulcanizates containing Koresin® and Technic KR -140

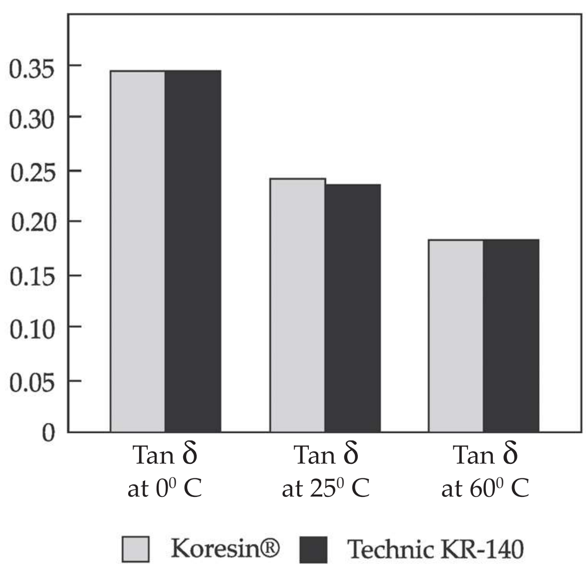

Fig. 7. Hysteresis properties of Koresin® and Technic KR-140 resins

The tensile and hardness data also confirm that both Technic KR-140 and Koresin® could perform similar in their applications.

Hysteresis properties

The tan δ values measured at different temperatures using a DMA instrument is shown in Fig. 7.

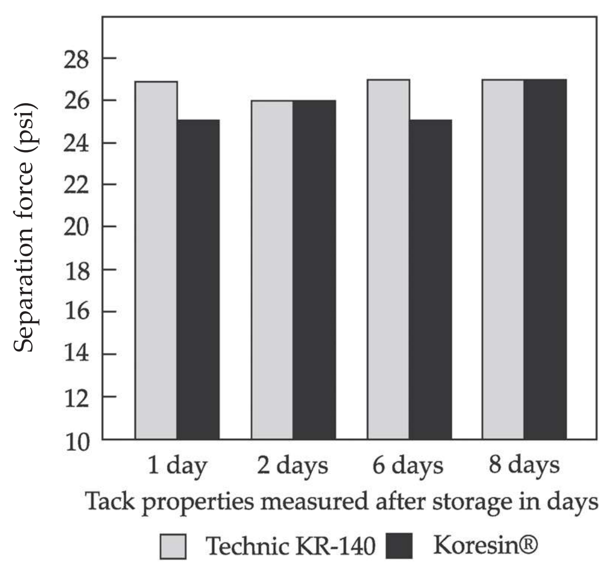

Fig. 8. Tack Performance (Tel-Tak Method) of Technic KR-140 against Koresin®

Table 6. **Tensile properties**

Property	Test Method	Koresin®	Technic KR-140
100% Modulus, MPa		3.4 (232)	3.6 (225)
300% Modulus, MPa	ASTM D 412	14.2 (—)	14.8 (—)
Tensile strength MPa		18.1 (64)	18.8 (63)
Elongation %		381(37)	380 (36)
Hardness, Shore A	ASTM D 2240	72 (+7)	72 (+8)

Values in (pararithesis) indicate per cent retention after ageing at 105 °C for 3 days.

In general, the tan δ property is the ratio of viscous contribution to the elastic contribution when a viscoelastic rubber subjected to dynamic deformations. Hysteresis is the heat loss when it is being deformed. Lower tan δ values indicate the lower heat buildup properties of a rubber compound. In the case of tyre tread compounds, DMA testing has shown that increased tan δ values at 0 °C temperature correlate to improved wet traction of tyres. Conversely, lower tan δ at 60 °C correlates to improved rolling resistance of tyres.

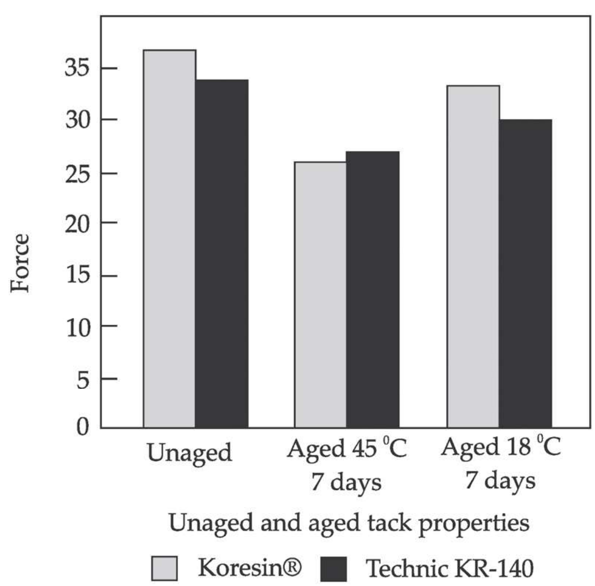

Fig. 9. Tack performance (Hasetri Test Method) of Technic KR-140 against Koresin®

The DMA tan δ values obtained for Technic KR-140 and Koresin® showed similar performance in compound properties. Since Koresin® is predominantly used in the manufacture of tyres and rubber articles, due to similar performance, Technic KR-140 could easily replace Koresin® in all its applications.

Evaluation of tack

The tack properties of Technic KR-140 were determined by Tel-Tak and HASETRI (JK Tyre) methods. Figs. 6 and 7 summarize the data obtained from these two methods.

Tel-Tak tack data (Fig. 8) was obtained from the rubber compound stored at room temperature for eight days. As expected, due to Koresin® type structure, Technic KR-140 resin retained its high tack properties in the compound even after 8 days of storage. Another set of tack testing data is given in (HASETRI rubber testing lab) Fig. 7. Here, in addition to unaged tack (after 24h of compounding), high (45 °C) and low temperature (18 °C) tack properties were determined. Again, these aged tack data also clearly confirmed that Technic KR-140 resin showed performances similar to Koresin®. Technic KR-140 has registered high initial tack and (similar to Koresin®) retained its tack properties under the extreme temperature conditions.

CONCLUSION

Technic KR-140 resin is structurally *similar* to Koresin®. The tackiness, viscosity, scorch, softening point of Technic KR-140 is similar to Koresin®. Technic KR-140 has high initial tack and also retains the tackiness during storage. Technic KR-140 can replace Koresin® in all tyre applications like tread compound, tread cement, conveyor belts, v-belts, cable sheathing, lining materials etc.

ACKNOWLEDGEMENT

The author would like to thank the management of TWC Group / Techno WaxChem Pvt Ltd, Mr. Sushil Agarwal, Mr. Abhishek Agarwal and Mr. Ashish Agarwal for continued support and encouragement to publish this work. My special and sincere thanks to Mr. Debanjan Dhar, Manager of R&D and Manufacturing at Techno WaxChem Pvt Ltd, Kolkata for his effort to commercialize the resin successfully.

REFERENCES

Banach, T.E., Howard, L.S., Pearsall, D.M., Knezevic, M. and Siudy, M.E. (2006). Modified novolac resin for use as tackifier. *US Patent application No 2006 / 0199924 A1.*

Beatty, J.R. (1969). Tel-Tak: A Mechanical Method for Estimating both Tackiness and Stickiness of Rubber Compounds, *Rubber Chemistry and Technology*, **42**(4): 1040-1053.

Busse, W.F., Lambert, J.M. and Verdery, R.B. (1946). Tackiness of GR-S and other Elastomers, *Journal of Applied Physics*, **17**: 376-385.

Galkiewicz, T.M., Petersen, K.C. and Sullivan, J.L. (1978). Tackifiers for elastomers. *US Patent No. 4073826.*

Gwin, L.E. and Weaver, E.J. (1977). A New Dimension in Rubber Compound Tackifiers, *Journal of Elastomers and Plastics*, **9**: 289-298.

Hamed, G.R. (1981). Tack and Green Strength of Elastomeric Materials, *Rubber Chemistry and Technology*, **54**: 576 - 595.

Howland, L. and Tewksbury, L.B. (1949).Oxyalkylated derivatives of phenolisanic acid- formaldehyde resins. *US Patent No. 2485097.*

Hooker Chemical Corporation USA. (1967). *British Patent No 1092086.*

Koresin® - High Performance Tackifier for the Rubber Industry, BASF Company – Technical Product Bulletin, August 2006.

Groote, M.D. and Keiser, B. (1952). Derivatives of certain oxyalkylated phenol-aldehyde resins useful in coating compositions. *US Patent No 2610955*.

Groote, M.D. and Keiser, B. (1951). *US Patent No* 2560333.

Groote, M.D. (1950). *US Patent No 2499365.*

Groote, M.D. (1950). *US Patent No 2499368.*

Groote, M.D. and Keiser, B. (1950). Process for breaking petroleum emulsions. *US Patent No 2499370.*

Magnus, F.L. and Hamed, G.R. (1991). Role of Phenolic Tackifiers in Polyisoprene Rubber, *Rubber Chemistry and Technology*, **64**(1): 65-73.

Marvel, C.S., Gander, R.J. and Chambers, R.R. (1949). Koresin and Related Resins, *Journal of Polymer Science*, **4(6)**, 689 – 702.

Schenectady Chemical Company, USA. (1967). *British Patent No. 1079909.*

Schmidt, M., Kemperman, T., Fries, H. and Esch, E. (1981). Resins based on novolaks, their production and other use as tackifiers. *US Patent No 4260704.*

Vredenburgh, W.A. and Hollis, S.D. (1972). Alkylphenol aldehyde resins. *US Patent No. 3674 723.*

Zoss, A.O., Hanford, W.E. and Schildknecht, C.E. (1949). *Industrial and Engineering Chemistry*, **41**, 74.