Technical

Cost-effective plasticizers in hose making

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A new growing trend is the use of renewable raw materials in rubber compounding.

This "green" concept is driven not only by the environmental concerns, but also by reduced cost structure of renewed raw materials.

For example, 65 to 70 percent lube oils are generated as waste, resulting in an environmental hazard if not recycled and brought back to use.

TECHNICAL NOTEBOOK
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Earlier some studies[1] in its use as process oil in rubber mats had been reported. Here, we report our studies on the cost reduction of extruded products by use of:

i) Vacuum re-refined oil on EPDM heater hose (RHC 41 percent) and radiator hose compound (RHC 29 percent);

ii) Cashew nut shell oil (CNSL) (CAS No. 8007-24-7) in NBR and NBR-PVC fuel resistant compounds;

iii) Effects of using both CNSL and re-refined oil in CSM cover compound.

Plasticization of polymers changes both technological and processing properties of polymers. Many theories were presented to explain the physical effects of plasticizers on polymer matrix.[1,2,3,4]

However, in short, plasticizers are able to dissolve the polymer (or induce swelling) while not entering into chemical reaction with it, i.e. they form a homogenous system.

So compatibility and solubility are important factors. Here, some study results were presented from author's earlier publication.[5,6]

Executive summary

A new compounding approach is needed to make good hoses at lower prices. Use of cost effective plasticizers is an effective way of reducing cost. In this study, we have presented the effects of some cost-effective substitution of plasticizers on physical as well as extruded properties. The outline of our work is as follows:

1. EPDM: Part and full substitution of original process oil with refined oil was studied in a) 41 percent RHC formulation; b) 29 percent RHC formulation;

2. NBR and NBR-PVC: Substitution of DOP and TP95 with CNSL and CNSL+ MRX mixture in fuel hose compounds were presented;

3. CSM: Studied effects of five plasticizers: DOP, DOA, CNSL, RE-REFING OIL and MRX.

In the case of an EPDM compound of 41 percent RHC, even 100 percent substitution of paraffinic refined oil by re-refined oil resulted in almost equal physical properties. Moreover, both the rate of extrusion and the die swelling were observed slightly lower with re-refined oil. Product test reports such as heat aging, coolant aging, oil swelling and low temperature properties (-40°C) of both oils were almost the same.

When 82 phr paraffinic oil in a low cost EPDM compound (29 percent) was gradually replaced by re-refined oil, the ML had reduced, but (Mh-ML), i.e. crosslink density, remained the same. While tensile strengths (heat, coolant and ASTM No. I oil aged) remained similar, all elongations of re-refined oil compounds were higher. The addition of 11 phr MRX had resulted in lower original and aged tensile strength with higher scorch time and better extrusion finish.

In an earlier study,[1] the author had presented CNSL substitution (CAS No-8007-24-7) in the fuel resistant NBR-hose compound. The substitution of DOP and TP95 by CNSL had resulted in slightly lower (~10 percent) tensile strength (both initial and fuel aged), but higher elongations, and higher volume swelling in fuels. Increasing accelerator by ~10 percent improved compression set and fuel aged properties. One interesting observation was the positive volume swell in ASTM No. 1 and No. 3 oils with good oil aged properties.

In CSM cover compounds, part or full substitution with refined oil resulted in significantly lower Mh and considerable under-curing of the compound. On the other hand, tensile strength and compression set properties were equal when CNSL was used to substitute DOP. Heat aging results were also the same.

But volume swelling in ASTM oils was higher and consequently hardness lower. With solo CNSL compound, extrusion speed was lower, possibly due to higher Mooney viscosity. It also resulted in cure bits and abnormal high head pressure. In CSM, the best all-around results were obtained with DOA.

Eventually, in all these substitutions, some cost reduction was achieved. Many such alternate plasticizers can be studied, and cost reductions can be implemented.

The author

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Bhattacharya

Bhattacharya received his doctorate in 1979 from Calcutta University. He has worked in the footwear and rubber automobile component industries much of his career, mostly in research and development.

Bhattacharya's work has been published in eight publications, mostly in international journals. He has made numerous presentations at a variety of rubber international conferences.

Experimental

Regular factory formulations were used. All materials were pre-approved as per raw material specification of the factory.

Master batches were made in a 75 liter dispersion kneader as per standard work procedure of that particular compound.

But no plasticizer was added in the master batch. Different portions of the master batch were weighed and the plasticizers were mixed in them on a 16"×42" mixing mill. Accelerators were added the next day. All tests were done as per ASTM procedures.

Extrusion studies were done on selected compounds using cold feed factory extruders. Die swell, rate of extrusion, visual finish, and head pressure were noted.

Hoses were vulcanized in direct steam autoclaves. The cure time was 30 minutes after the steam pressure was achieved. Final hoses were subjected to final product tests. All results were recorded and reported with comparative chart.

Results and discussion

Study on EPDM was carried with two types of formulations: a) A polymer rich heater hose formulation of 41 percent RHC; b) highly loaded radiator hose formulation having 29 percent RHC. The results of heater hose formulation with 41 percent.

RHC was presented in **Figs. 1-4**. We observed that tensile strength, compression set and hardness remained unchanged during replacement of paraffinic oil with re-refined oil.

Though aged tensile strengths remained the same (**Fig. 2**), aged elongations were higher (**Fig. 3**). Extrusion results (**Fig. 4**) indicated equal die swelling and higher extrusion rate with re-refined oil. Heat, coolant, and low temperature aging (-40°C) results of products were found equal.

As most of the EPDM compounds are heavily loaded, it would be interesting to observe the results presented in **Table 1** and **Fig. 5** where 82 phr paraffinic oil gradually was replaced (partially and totally) by re-refined oil. Hardness and tensile strengths (heat, coolant or ASTM No. I oil) remained equal; but all elongations were higher in re-refined oil compounds (B and C).

In Rheo studies on accelerated compounds, we observed slight drop in both Ml (~10 percent), and Mh in both (B) and (C).

However, (Mh-Ml), Ts^2 and T90 remained almost the same. Interestingly, use of 11phr MRX in place of oils (D), reduced the tensile strength (both initial and aged), but increased elongations

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Table1. Effect of plasticizers on physical properties of EPDM hose (29 percent).

ELASTO/REFINED	82/0 (A)	41/41 (B)	0/82 ©	35/35/12(MRX)(D)
Original Ts	152	151	153	140
Heat aged Ts	134	142	139	122
Coolant aged Ts	149	152	136	126
ASTM#1 aged Ts	117	122	115	102
Original Eb	376	376	403	500
Heat aged Eb	203	218	225	280
Coolant aged Eb	312	330	298	400
ASTM#1 aged Eb	290	312	298	385
Compression set	50	54	53	55
Hardness	72	70	73	71
Heat aged Hs	76	75	78	76
Vol. change#1Oil	58	61	61	64

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and Ts^2 substantially.

The rate of extrusion, die swell and finishing of extruded hose were best in MRX blended compound (D), followed by (C), 82 phr re-refined oil. The physical properties of (A) and (B) were almost the same.

NBR

Di-octyl phalate (DOP), the most widely-used plasticizer in NBR, is now placed under a negative list of REACH protocol. The widely used ester plasticizers (such as TP 95) are very costly.

In this background, we considered whether it was worth it to study[5,6] the effects of substituting both DOP and TP 95 by a low-cost plasticizer, cashew nut shell oil (CNSL) in a typical NBR formulation to meet international fuel hose standard JAE S-30 R7.

Comparing tensile strength, it may be noted from **Fig. 6** that CNSL compounds had a 15 percent lower initial, heat and ASTM oil No. 3 aged tensile strength, while fuel aged strengths were 58-63 kg/cm^2 i.e. 5-10 percent lower than TP95 or DOP compounds.

However, the opposite picture was observed in elongation values. It was highest in solo CNSL compound, followed by mixed (CNSL+ TP95) plasticizers (C4).

Hardness after fuel aging (**Fig. 7**) is lower in CNSL containing compounds (C3 and C4) due to higher volume swelling.

We had observed (**Fig. 8**) reduction in (Mh-Ml) values in CNSL compounds (C3 and C4), resulting in increased compression set values. So we added 10 percent more accelerators in C3. The resulting compound (C5) had increased (Mh-Ml) and improved compression set.

Figs. 10 and 11 present the effects of plasticizers, as shown, in a CSM cover compound. Tensile strength was found to be highest in CNSL compounds, but elongation and hardness values of all plasticizers were very close (**Fig. 9**).

Also, CNSL compound had the highest (Mh-Ml). This resulted in high extrusion speed (**Fig. 11**) among all the plasticizers studied. However, the die pressure was very high, and scorch particles were formed within a short time. Mooney viscosity was also high.

The compound with DOA, on the other hand, had the lowest Mooney viscosity, good extrusion speed and medium die swelling. So the direct substitution of DOP with CNSL was not possible. Refined oil resulted in very low Mh, and even slab making was not possible.

Mixture with MRX also had low Mh-Ml values (**Fig. 10**).

Summary

In this study, we have presented the effects of some cost-effective substitution of plasticizers on physical as well as extruded properties.

In the case of the EPDM compound (both 41 percent and 29 percent RHC), even the 100 percent substitution of paraffinic oil by re-refined oil resulted in almost equal physical and product properties.

Moreover, both the rate of extrusion and die swelling had improved slightly with re-refined oil.

The product test report, such as heat aging, coolant aging, oil swelling and low temperature properties (-40°C) of both oils were almost the same.

Substitution of both the DOP and TP95 with CNSL was studied in an NBR fuel hose compound. Though tensile properties were slightly lower, the

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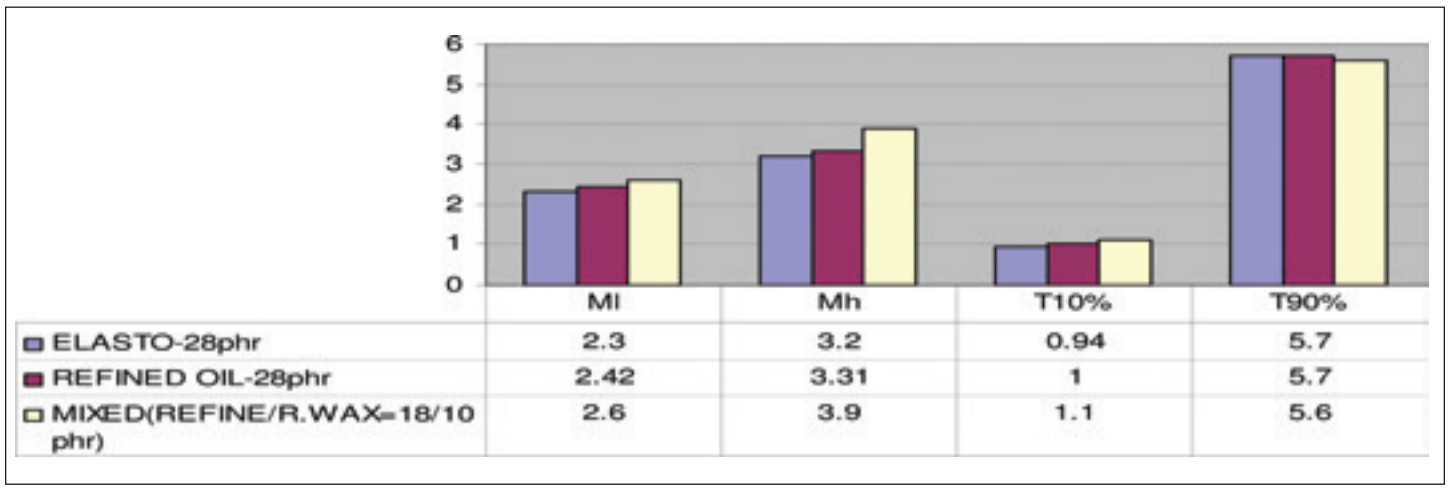
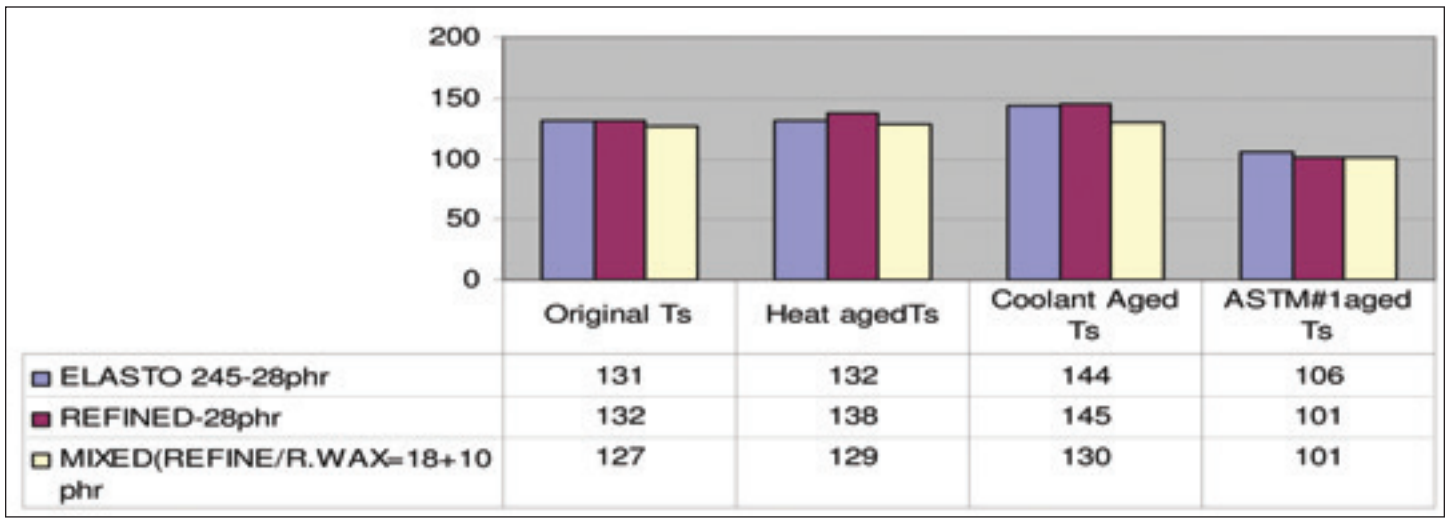
Fig 1. Effect of plasticizers on rheometer properties in EPDM hose (41 percent RHC).



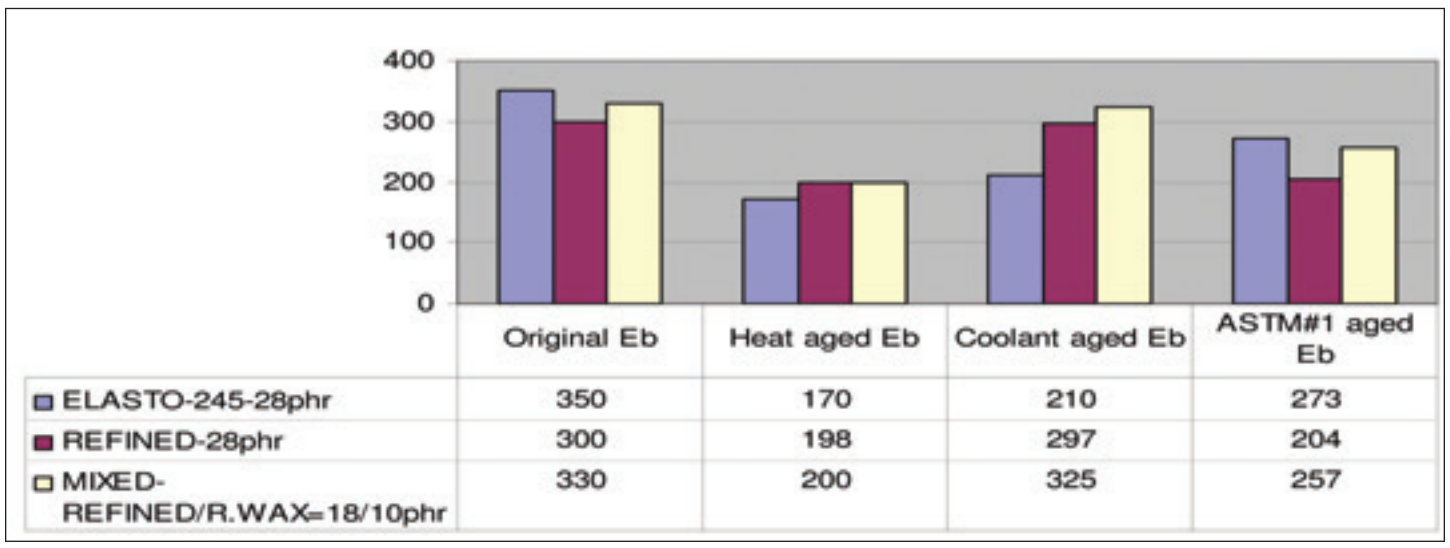
	Ml	Mh	T10%	T90%
ELASTO-28phr	2.3	3.2	0.94	5.7
REFINED OIL-28phr	2.42	3.31	1	5.7
MIXED(REFINE/R.WAX=18/10 phr)	2.6	3.9	1.1	5.6

Fig. 2. Effect of plasticizers on tensile strength in EPDM hose (41 percent RHC).



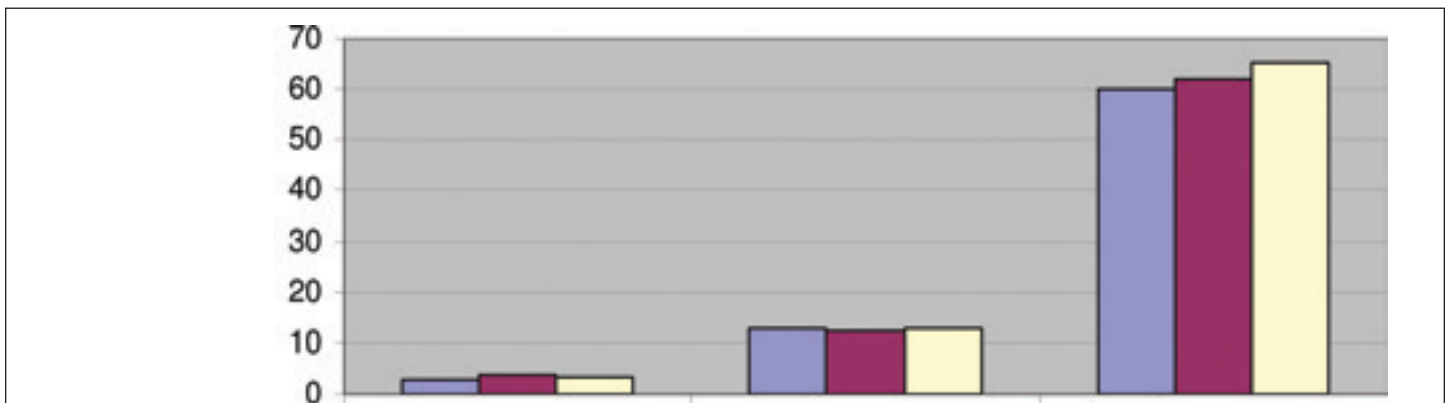
	Original Ts	Heat agedTs	Coolant Aged Ts	ASTM#1aged Ts
ELASTO 245-28phr	131	132	144	106
REFINED-28phr	132	138	145	101
MIXED(REFINE/R.WAX=18+10 phr	127	129	130	101

Fig 3. Effect of plasticizers on elongation properties of EPDM hose (41 percent RHC).



	Original Eb	Heat aged Eb	Coolant aged Eb	ASTM#1 aged Eb
ELASTO-245-28phr	350	170	210	273
REFINED-28phr	300	198	297	204
MIXED-REFINED/R.WAX=18/10phr	330	200	325	257

Fig. 4: Effect of plasticizers on extrusion properties of EPDM hose (41 percent RHC).



	Extrusion Speed(Kg/hr)	Die Swell(%)	Mooney Viscosity(125°C)
Paraffinic oil(28phr)	2.75	12.7	60.2
Re-Refined oil(28phr)	3.6	12.3	61.9
Mixed(14+14phr)	3.2	12.6	65.1

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An *RPN* call for papers

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elongation, and the volume change in ASTM No. 1 and No. 33 oils were superior. Fuel aged properties were also very near.

Low temperature resistance properties, tested on the product, were equal. In a CSM cover compound, substitution of DOP with CNSL had resulted in higher tensile strengths, equal hardness, elongation, ASTM oil swelling, low temperature and ozone properties.

Extrusion, however, was not successful due to high head pressure and scorching. DOA was found to be a better substitute with lower Mooney viscosity, equal speed and low head pressure. More studies were needed.

Eventually, in all these substitutions,

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Fig. 5. Effect of plasticizers on physical properties of EPDM hose (29 percent).

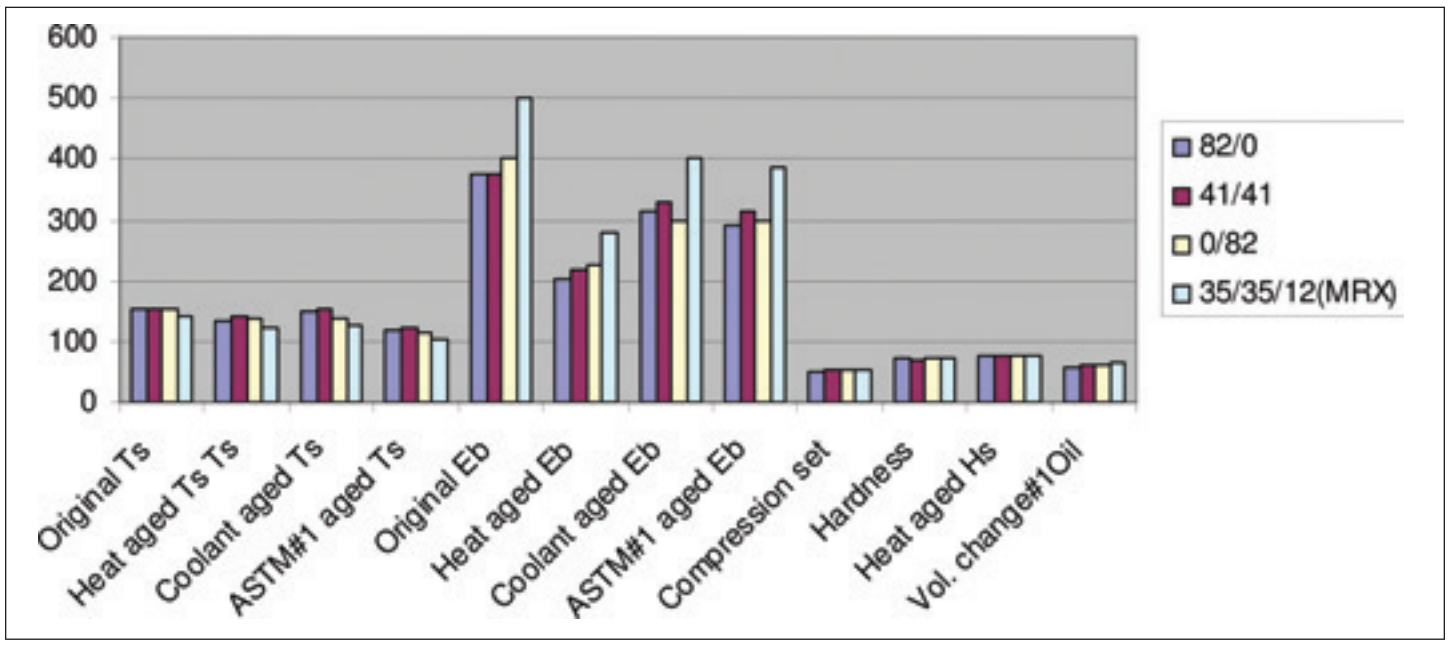
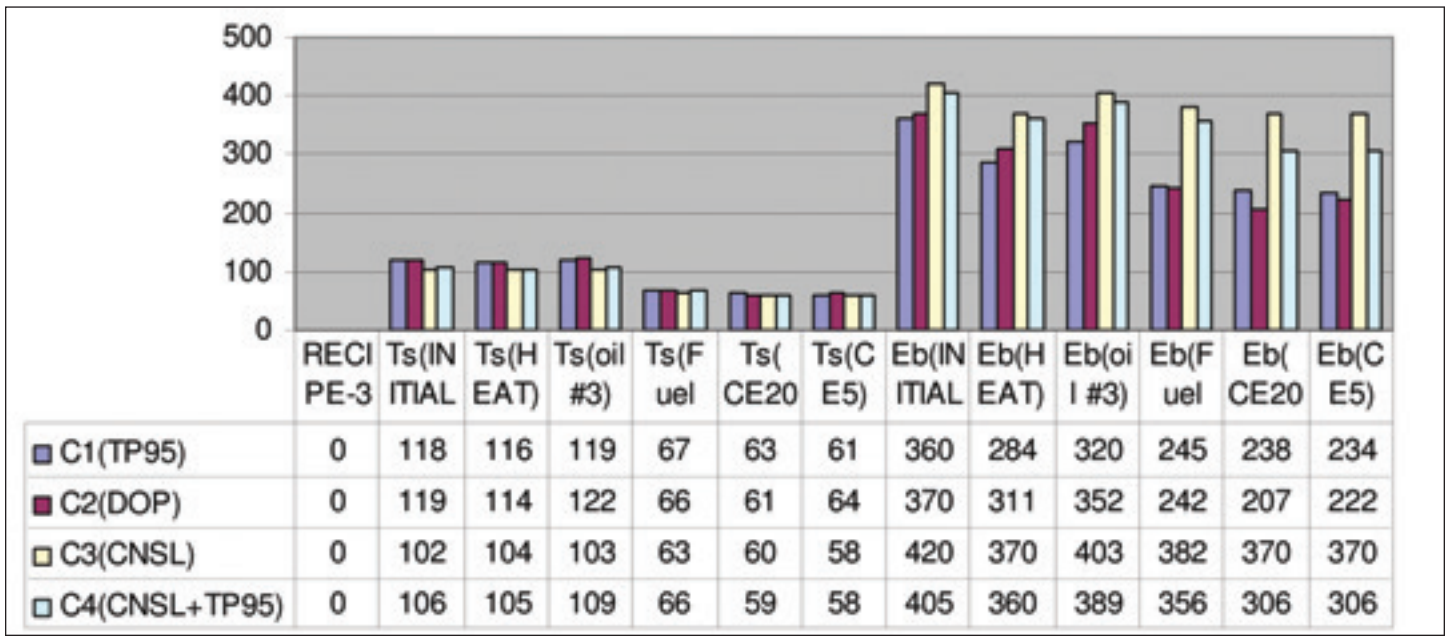
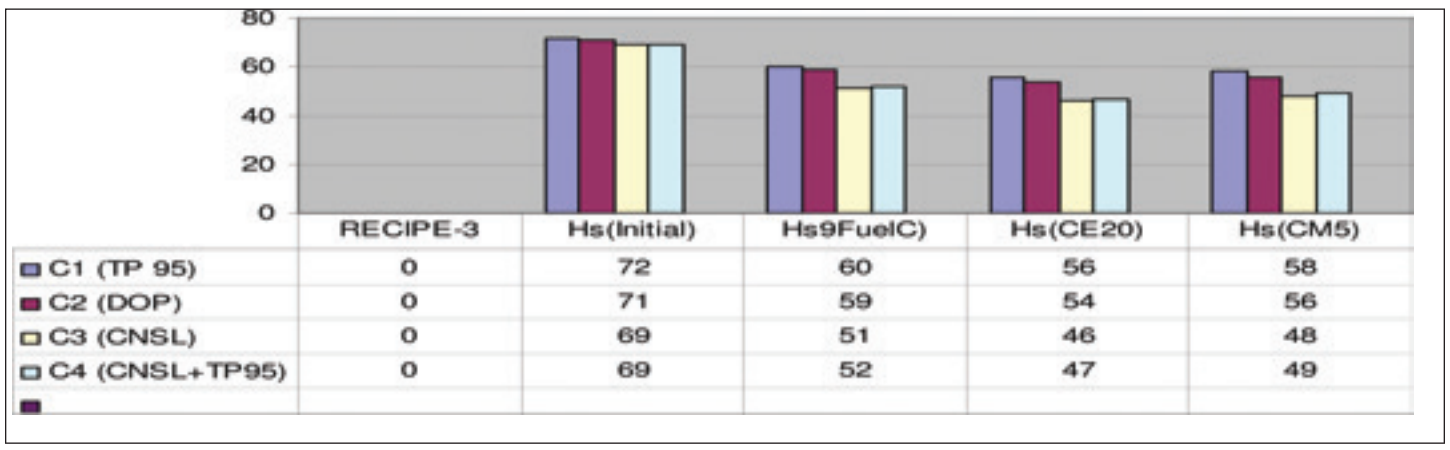


Fig. 6. Comparison of initial and aged tensile strengths (kg/cm²) in NBR fuel hose.



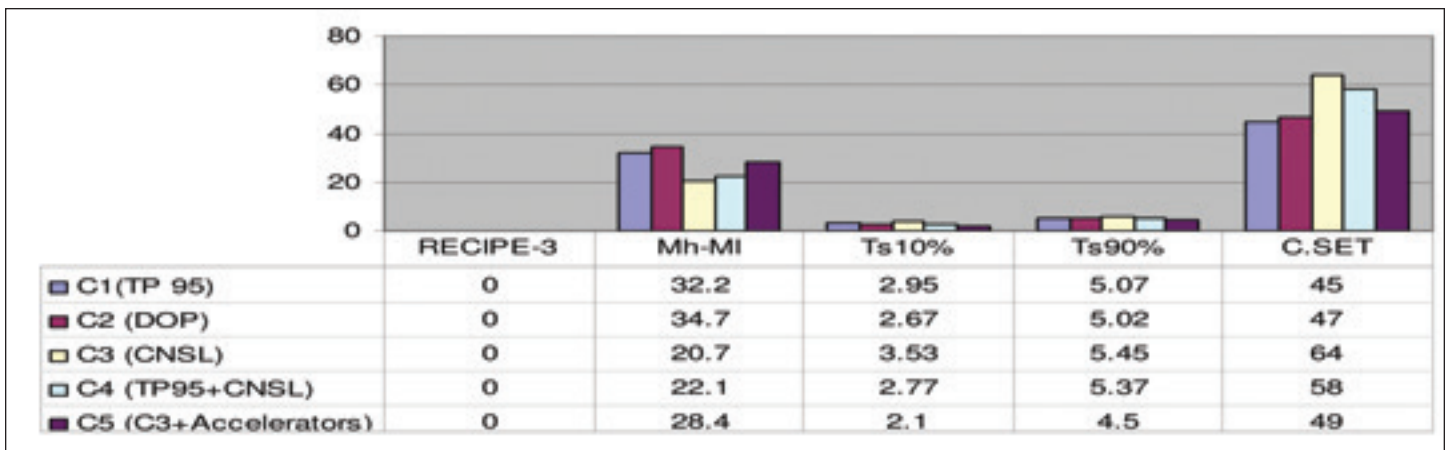
	RECIPE-3	Ts(INITIAL	Ts(HEAT)	Ts(oil #3)	Ts(Fuel	Ts(CE20	Ts(CE5)	Eb(INITIAL	Eb(HEAT)	Eb(oil #3)	Eb(Fuel	Eb(CE20	Eb(CE5)
C1(TP95)	0	118	116	119	67	63	61	360	284	320	245	238	234
C2(DOP)	0	119	114	122	66	61	64	370	311	352	242	207	222
C3(CNSL)	0	102	104	103	63	60	58	420	370	403	382	370	370
C4(CNSL+TP95)	0	106	105	109	66	59	58	405	360	389	356	306	306

Fig 7: Comparison of initial and fuel aged hardness in fuel hose compound.



	RECIPE-3	Hs(Initial)	Hs9FuelC)	Hs(CE20)	Hs(CM5)
C1 (TP 95)	0	72	60	56	58
C2 (DOP)	0	71	59	54	56
C3 (CNSL)	0	69	51	46	48
C4 (CNSL+TP95)	0	69	52	47	49

Fig 8: Comparison of rheometer (ODR), properties and compression set in fuel hose.



	RECIPE-3	Mh-Ml	Ts10%	Ts90%	C.SET
C1(TP 95)	0	32.2	2.95	5.07	45
C2 (DOP)	0	34.7	2.67	5.02	47
C3 (CNSL)	0	20.7	3.53	5.45	64
C4 (TP95+CNSL)	0	22.1	2.77	5.37	58
C5 (C3+Accelerators)	0	28.4	2.1	4.5	49

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Master Bond Inc. said its EP21AOLV-2Med is often selected for bonding, sealing, coating and encapsulation applications in the medical device industry because of its biocompatibility and cytotoxicity certifications.

The EP21AOLV-2Med is a two-component epoxy system that withstands a variety of sterilization methods, including EtO, radiation and many cold sterilants.

EP21AOLV-2Med is thermally conductive and electrically isolating with a smooth consistency and good flow properties, Master Bond said, and it bonds well to metals, composites, glass, ceramics, plastics and many rubber materials.

Products

The system offers a high tensile modulus of 450,000-500,000 psi, strength exceeding 18,000 psi and very low shrinkage upon curing. Master Bond said EP21AOLV-2Med has a shelf life of six months in its original, unopened containers.

More about Master Bond's systems is available at www.masterbond.com.

TLV's VS3 Air Vent

TLV Corp. has developed VS3 Air Vent for sanitary applications, which broadens TLV's series of stainless steel products for use with sanitary applications needing an air vent for a liquid line or filter.

Three-point seating and a rubber valve seat allow for tight sealing of TLV's Free Float, TLV said, and VS3 meets specific requirements for materials, surface treatments, component configuration and industry standards set by the FDA and USP.

For information, go to www.tlv.com.

Stratasys Ltd. has introduced the Objet500 Connex1 and Objet500 Connex2 Multi-material 3D Printers featuring the company's triple-jetting technology.

Stratasys said its triple-jetting technology is designed to allow the user to build products with up to three different materials in a single run or even mix multiple material droplets to form new digital materials such as tough Digital ABS.

The Objet500 Connex1 is equipped with a large build envelope and can produce parts from three diverse materials in a single production run, the company claimed. This allows users to create assemblies with components formed from three different materials, the company said, or it can produce components that contain both rigid and flexible materials. The 3D printer can build a part up to 19.3 in. x 15.4 in. x 7.9 in. or a mixed tray of small parts.

The 3D Printer enables users to combine transparency, durability and flexibility in one part, Stratasys said. It can combine droplets from two base materials to produce new materials or digital materials.

For more information,visit the Stratasys website at www.stratasys.com.

Sick Inc. has launched the AHS/AHM36 absolute encoders, singleturn and multiturn encoders that have a 270-degree rotating M12 connector or cable outlet that enables flexible, time-saving installation in limited spaces, according to the company.

The encoders have a small diameter at 36 mm. Face mount flange, servo flange and blind hollow shaft versions are available, Sick said, each with five different shaft diameters and various adapters. Sick claims the encoders are fully magnetic and are able to withstand dust, water jets and temperatures from -40°C to 100°C.

With an enclosure rating up to IP 67, Sick said AHS/AHM36 encoders are suited for automated guided systems, industrial vehicles and utility vehicles, but they can be used in packaging machines, logistics applications and machine building.

Go to www.sickusa.com for more info.

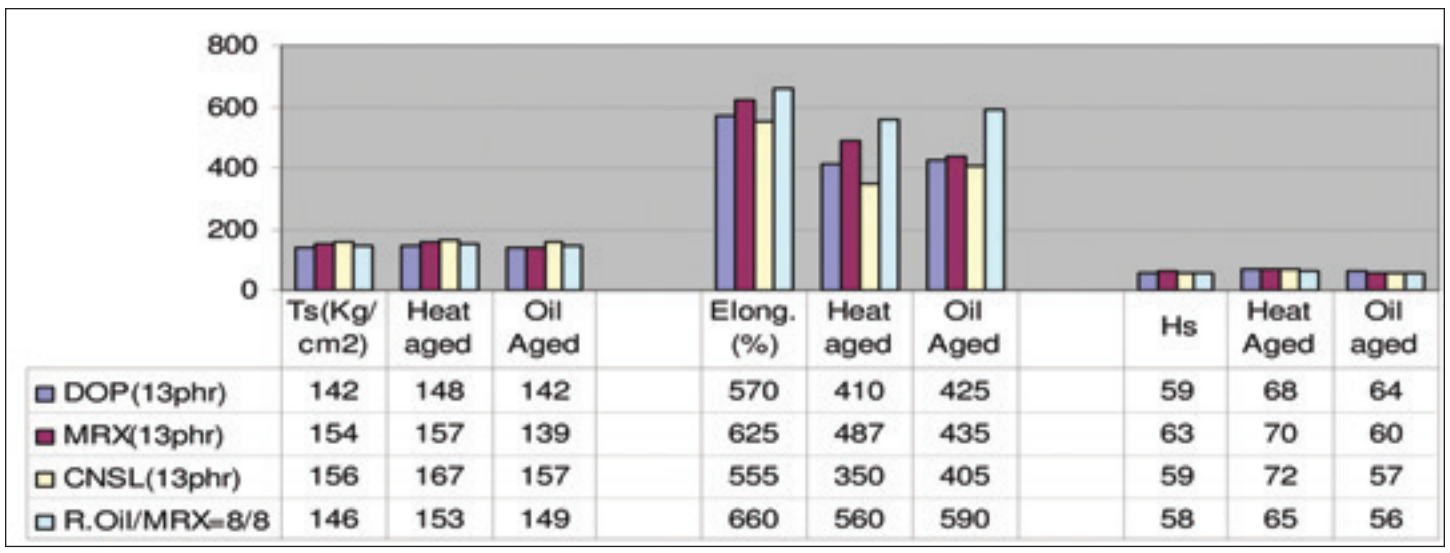
Huntsman Corp. has developed two UV protected grades of thermoplastic polyurethanes for offshore, oil and gas, and mining wire and cable applications: Irogran A 85 P 4394 UV DP, with a hardness of 85 Shore A; and Irogran A 92 P 4637 UV DP, with a hardness of 92 Shore A.

The polyether-based TPU materials are designed for jacketing the cables of heavy duty pieces of equipment because they have to function in harsh, abrasive and outdoor environments and are exposed to the elements. Over time, exposure to ultraviolet light can cause cabling materials to degrade, Huntsman said, losing performance in tensile strength, abrasion and elongation. On oil rigs, offshore wind farms and in underground applications, any form of deterioration in cable quality is unacceptable and could have costly consequences, it said.

Huntsman said these grades were developed in response to requests from customers in the Americas, who were asking for increasingly demanding performance levels from their cable jacketing materials.

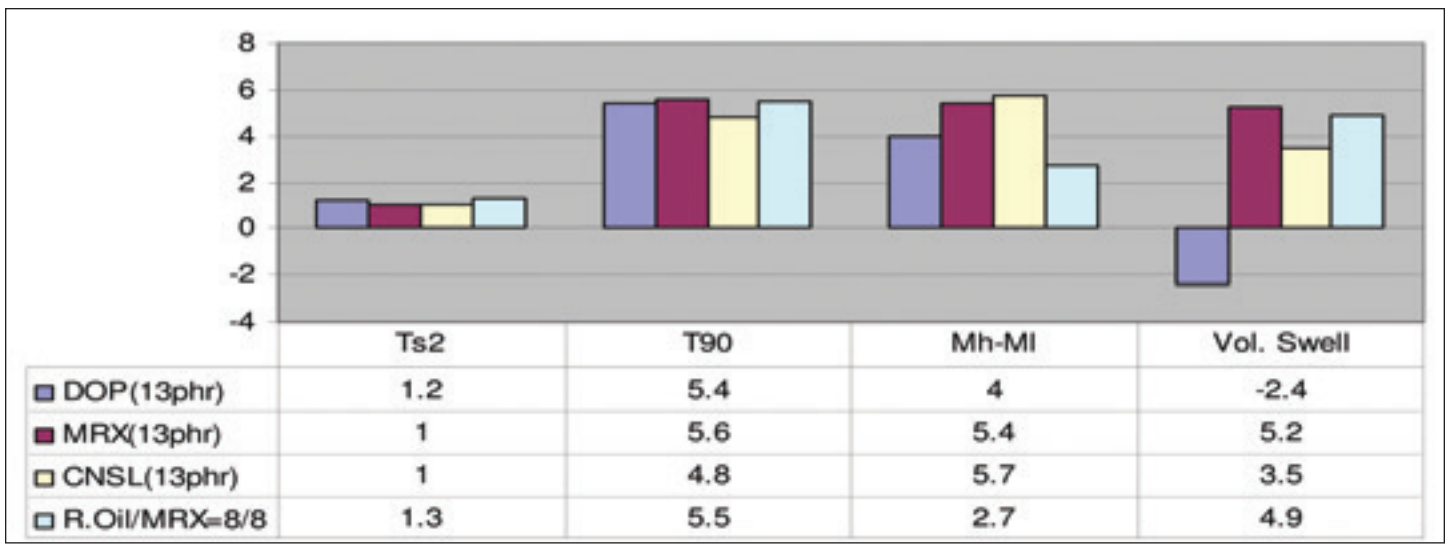
For more information, go to www.huntsman.com.

Fig. 9. Effect of plasticizers on CSM cover compound.



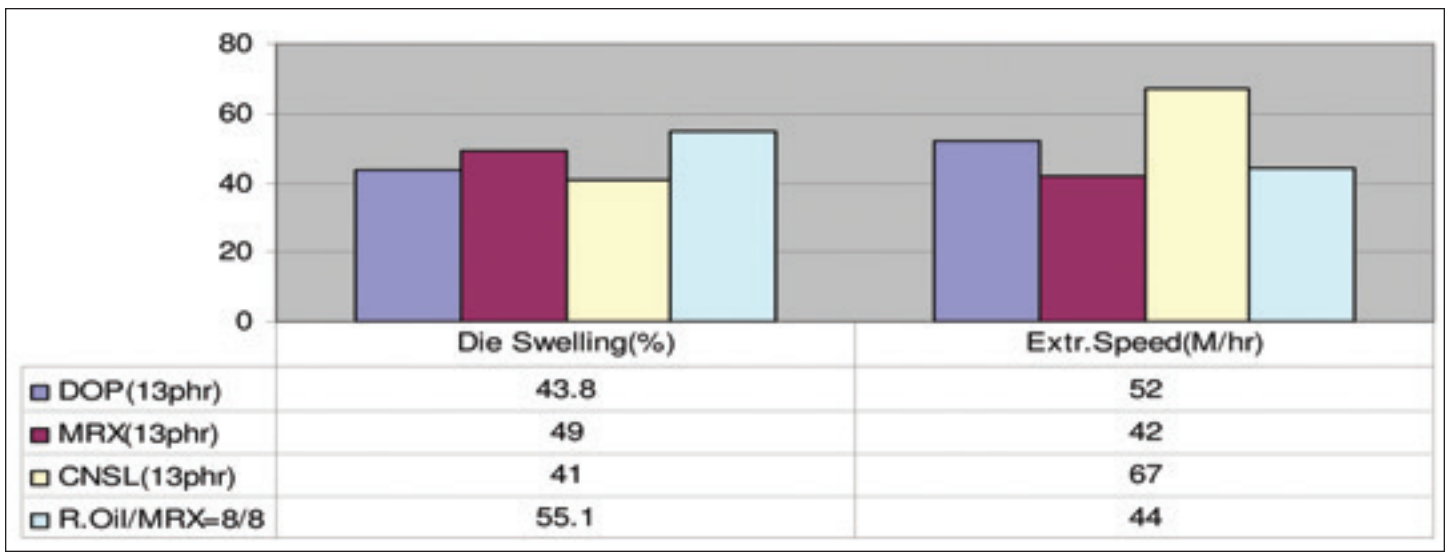
	Ts(Kg/cm2)	Heat aged	Oil Aged	Elong. (%)	Heat aged	Oil Aged	Hs	Heat Aged	Oil aged
DOP(13phr)	142	148	142	570	410	425	59	68	64
MRX(13phr)	154	157	139	625	487	435	63	70	60
CNSL(13phr)	156	167	157	555	350	405	59	72	57
R.Oil/MRX=8/8	146	153	149	660	560	590	58	65	56

Fig. 10. Effect of plasticizer in Hypalon cover compound.



	Ts2	T90	Mh-Ml	Vol. Swell
DOP(13phr)	1.2	5.4	4	-2.4
MRX(13phr)	1	5.6	5.4	5.2
CNSL(13phr)	1	4.8	5.7	3.5
R.Oil/MRX=8/8	1.3	5.5	2.7	4.9

Fig. 11. Effect of plasticizers on extrusion properties of CSM cover.



	Die Swelling(%)	Extr.Speed(M/hr)
DOP(13phr)	43.8	52
MRX(13phr)	49	42
CNSL(13phr)	41	67
R.Oil/MRX=8/8	55.1	44

Hose

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some cost reduction was achieved. Many such alternate plasticizers can be studied and cost reductions can be implemented.

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