DETERMINATION OF THE EFFECT OF ACCELERATOR TYPE AND ACCELERATOR/SULFUR RATIO ON THE VULCANIZATION KINETICS AND AGING PROPERTIES OF NATURAL RUBBER/CHLOROPRENE BASED RUBBER COMPOUNDS

DOĞAL KAUÇUK/KLOROPREN KAUÇUK ESASLI KARIŞIMLARIN VULKANİZASYON KİNETİĞİNE VE YAŞLANMA ÖZELLİKLERİNE HIZLANDIRICININ TİPİNİN VE HIZLANDIRICI/KÜKÜRT ORANININ ETKİSİNİN BELİRLENMESİ

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This work named **"Determination of The Effect of Accelerator Type and Accelerator/Sulfur Ratio on The Vulcanization Kinetics and Aging Properties of Natural Rubber/Chloroprene Based Rubber Compounds"** by **FARZAD AHMADZADEH NOBARI AZAR** has been approved as a thesis for the Degree of **DOCTOR OF PHILOSOPHY IN CHEMISTRY** by the below mentioned Examining Committee Members.

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☐ **Serbest Seçenek/Yazarın Seçimi**

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(İmza)

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ETHICS

In this thesis study, prepared in accordance with the spelling rules of Institute of Graduate Studies in Science of Hacettepe University.

I declare that

- all the information and documents have been obtained in the base of the academic rules
- all audio-visual and written information and results have been presented according to the rules of scientific ethics
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- all cited studies have been fully referenced
- I did not do any distortion in the data set
- and any part of this thesis has not been presented as another thesis study at this or any other university.

16/06/2017

FARZAD AHMADZADEH NOBARI AZAR

ABSTRACT

DETERMINATION OF THE EFFECT OF ACCELERATOR TYPE & ACCELERATOR/SULFUR RATIO ON THE VULCANIZATION KINETICS AND AGING OF NATURAL RUBBER/CHLOROPRENE BASED RUBBER COMPOUNDS

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In the scope of this thesis it has been tried to clarify the effects of different types of accelerators and the effects of accelerator/sulfur ratio also known as vulcanization system on mechanical, thermo mechanical and stress relaxation properties, crosslink density and network structure of the NR/CR vulcanizates. In addition, it has been tried to clarify effects of accelerator type and vulcanization system on accelerated weathering behavior of NR/CR based elastomers method has been chosen to investigate aging behavior in conditions closer to open air, where NR based materials are more vulnerable to aging. So far, such relationship has not been established to identify the effects of type and ratio of accelerator used in preparation of NR/CR based elastomers on crosslink density and aging properties of the resulting vulcanizates using pulse-NMR technique and spin-echo method and the role of dynamic relaxation after accelerated weathering. It has been planned to fill this gap in the literature and provide detailed scientific data related to structural differences of sulfur vulcanizates and their thermo mechanical response to different cure systems.

The ultimate goal of this thesis is to determine optimum accelerator, and accelerator/sulfur ratio for not pre-scorched but fast vulcanized, minimum reversion vulcanizates, which possess stable mechanical properties and crosslink density even after curing. For this purpose, keeping all the other chemicals in a fixed amount, we have prepared a series of compounds in an internal mixer using tetramethyl thiuram disulfide (TMTD), 2-Mercaptobenzothiazole (MBT), diphenyl guanidine (DPG), Zinc dibutyl dithiocarbamate (ZDBC) and N,N' Diethylthiourea (DETU) from different types of accelerators and also different accelerator to sulfur ratios.

The vulcanization of the compounds has been examined by using moving die rheometer (MDR); crosslink densities have been determined by pulse-NMR technique; stress relaxation properties have been analyzed using temperature scanning stress relaxation (TSSR) method; and mechanical properties have been determined by universal testing machine.

To determine weathering effect, the prepared vulcanizates have been aged using accelerated weathering machine. Changes in thermal, mechanical and thermo-mechanical properties have been analyzed using the same standard methods in order to maintain a good comparison base.

At the end of all these experimental work, the relations between each accelerator group and each cure system and mechanical, thermal and thermo mechanical properties of the NR/CR based vulcanizates have been clarified. This will fill the literature gap in this field and provide valuable information for the researchers, students and engineers who are trying to prepare NR/CR based formulations with optimum thermal, mechanical, thermo-mechanical and aging properties.

Keywords: Natural Rubber, Chloroprene Rubber, Accelerated weathering, Pulse NMR, Temperature Scanning Stress Relaxation

GENİŞ ÖZET

DOĞAL KAUÇUK/KLOROPREN KAUÇUK ESASLI KARIŞIMLARIN VULKANİZASYON KİNETİĞİNE VE YAŞLANMA ÖZELLİKLERİNE HIZLANDIRICININ TİPİNİN VE HIZLANDIRICI/KÜKÜRT ORANININ ETKİSİNİN BELİRLENMESİ

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Kauçuk ilk defa 1840 'lı yıllarda çoğu kez kord bezi, pamuklu bez veya ipek ile birlikte sarılarak top, su geçirmez elbise ve ayakkabı yapımında kullanılmıştır. Yazın sıcakta yumuşayan, kışın soğukta donarak sertleşen bu malzemeler, kullanım sırasında sonunlar yaratmıştır. Pişmemiş(çapraz bağlanmamış) kauçuk çok yapışkan, kopma mukavemeti düşük ve kirleten malzeme görünümündedir. İlk defa Amerika'da Charles Goodyear kauçuğun kükürt ile karıştırılıp ısıtıldığında yapışkan olmayan, yüksek elastikliğe ve mekanik özelliklere sahip bir malzeme haline dönüştüğünü keşfetmiştir. Aynı yıllarda İngiliz Thomas Hancock da benzer çalışmalar yapmış; bu iki bilim insanı vulkanizasyonu keşfetmiş ve tüm dünyaya duyurmuşlardır.

Vulkanizasyon yani kükürt ile çapraz bağlanmanın keşfinden sonra dünyada kauçuk eşya kullanımı hızla artmıştır. Kükürt vulkanizasyonu ile elastomerlerin hazırlanması ilk yılarda sadece kükürt yardımı ile gerçekleştirilmiştir. Yapılan araştırmalar sonucunda sırasıyla metal oksitlerin (ör: çinko oksit) ve organik hızlandırıcıların vulkanizasyon hızını artırdığı tespit edilip, bu kimyasallar kauçuk reçetelerinde yer almaya başlamıştır. Bu maddeler hem vulkanizasyonu hızlandırmalarının yanı sıra mekanik özelliklerinin artmasını sağlamıştır. 1921 yılında bulunan merkaptobenzotriazol ilk ticari hızlandırıcı olarak kauçuk sanayiinde yerini almıştır. Bu hızlandırıcının kauçukta kullanılması

sonunda reçetelerde kükürt miktarı azaltılmış ve daha iyi yaşlanma performanslarına ulaşılmıştır.

Kauçuğun gündelik hayatta önemi ve kullanım alanlarının artmasıyla birlikte kauçuk bilimi ve teknolojisi alanlarında bilimsel çalışmalarını sayısı artmış ve başlangıçtaki basit görünen ve kauçuk ve kükürtten oluşan reçetelere farklı kimyasallar girilerek son ürünlerin mekanik, termo-mekanik ve yaşlanma özellikleri iyileştirilmiş ve maliyetleri düşürülmüştür. Siyah ve beyaz dolgu maddeleri (ör: karbon siyahları ve silikalar), yumuşatıcılar, antioksidantlar ve yağ asitleri bu kimyasalların en önemli örneklerinden olup günümüzde her kauçuk reçetesinin temelini oluşturmaktadırlar. Bu reçetenin üzerinde kauçuğun kullanım koşullarına ve amacına bağlı olarak şişirici, boya maddesi, koku maddeleri gibi katkılar katılabilmekte veya karbon siyahı dolgusu yerine silika gibi dolgu maddeleri kullanılabilmektedir.

Kauçuk reçeteleri son üründe aranan özelliklere göre tasarlanmaktadır. Her reçetesinin özelliklerinin önemli bir kısmı seçilen kauçuk türlerinden meydana gelmektedir. Miktar olarak reçetenin en büyük bileşeni olan kauçuklar kendilerine ait özelliklerinin önemli bir bölümünü son ürüne taşımaktadır. Nerdeyse tamamı cis-1,4 poli isoprenden oluşan doğal kauçuk, yüksek yapısal düzeni sebebiyle kristallenmeye meyilli bir kauçuk türüdür. Bu kristallenme doğal kauçuğun kopma dayanımı, aşınma ve yırtınma direnci gibi önemli özelliklerinin çok iyi olmasına sebep olmaktadır. Bu nedenle günümüzde fazla sayıda ve farklı özellikte suni kauçuk bulunmasına rağmen, doğal kauçuk hala dünya kauçuk tüketiminin büyük bir kısmını oluşturmaktadır. Ancak bu kauçuk oksidatif yaşlanmaya dirençsiz olup, oksijen veya ozon varlığında hızlı bozulmaya uğramaktadır.

Kloropren kauçuğu doğal kauçuk gibi yüksek yapısal düzene sahip olup bu nedenle de doğal kauçuğun çoğu özelliğini paylaşmaktadır. Ayrıca yapıda klor atomunun bulunması sebebiyle daha iyi yağ, sıcaklık ve yaşlanma direncine sahiptir. Tez kapsamında elde edilen sonuçların daha geniş bir alanda faydalı olması amaçlandığından, günümüzde birçok farklı alanda ve çok yaygın kullanılan bu kauçukların karışımı reçetede temel alınmıştır.

Bir reçeteyi oluşturan farklı kimyasallar içerisinde hızlandırıcılar çok önemli bir yere sahiptirler. Bunun başlıca sebebi hızlandırıcı türü ve miktarının işleme kolaylığından, ürünün ömür süresine kadar bir kauçuk ürününün neredeyse tüm özellikleri üzerindeki belirgin etkisidir. Hızlandırıcılar yukarıda belirtildiği gibi vulkanizasyon hızını arttırarak mamul özelliklerine olumlu etkiler yapan maddeler olarak tanımlanır. Faklı kimyasal yapıda olduklarından, vulkanizasyon sırasında farklı etkiler meydana getirirler. Organik hızlandırıcıların kükürtle birlikte kullanıldığı zaman çapraz bağlanma reaksiyonlarını hızlandırmasının, kısa süren ve ekonomik pişme oluşturmasının yanı sıra kauçuk ürünün ısıl dayanımı, dinamik özellikleri ve yaşlanma özelliklerinde önemli iyileşmeler sağlamıştır.

Hızlandırıcılar vulkanizasyon etkinliğine göre çok hızlı, orta hızlı ve yavaş olmak üzere üç grupta toplanabilir. Ditiyokarbamat ve Thiuramlar çok hızlı hızlandırıcılar sınıfındayken Merkaptolar ve Sülfenamidler orta hızlı hızlandırıcılardandır. Guanidinler ise yavaş hızlandırıcı olarak kullanılan hızlandırıcıların başında gelmektedir. Bu tez kapsamında farklı tip hızlandırıcılarının, doğal kauçuk/kloropren kauçuk karışımlarının mekanik, termo-mekanik ve yaşlanma özelliklerinin üzerindeki etkisinin incelenmesi amaçlandığından, TMTD, MBT ve DPG hızlandırıcıları sırasıyla hızlı, orta hızlı ve yavaş pişme etkinliğine sahip hızlandırıcı gruplarının temsilcisi olarak seçilmişlerdir. Bu hızlandırıcılar içerisinde TMTD hızlı pişirme etkinliği ve yüksek mekanik özelliklerinden dolayı uzun yıllardır sanayide sıklıkla kullanılan bir hızlandırıcıdır. Ancak son yıllarda yapılan araştırmalar sonucunda sağlık riskleri taşıyan nitrozamin oluşturduğunun kanıtlanmasından dolayı, TMTD kullanımına kısıtlamalar getirilmiştir. Bu nedenle yine yüksek pişirme etkinliğine ve iyi mekanik, termo-mekanik ve yaşlanma özelliklerine sahip olan ancak sağlık riski içermeyen alternatif hızlandırıcıların bulunmasının önemi artmıştır. Bu kapsamda tez kapsamında NR/CR karışımları için hızlı hızlandırıcılar sınıfından ZDBC ve DETU hızlandırıcıları seçilmiştir.

Bahsi geçen hızlandırıcıların kükürt vulcanizasyonu sonucunda oluşturdukları ağ yapısı içinde “tekli”, “ikili” ve “çoklu” sulfidik çapraz bağlanmaların dağılımı önemlidir. Polisülfidik bağların uzunluğunun dağılımı vulkanize yapının ısıl özelliklerini ve son özelliklerini etkileyen önemli bir parametredir. Polisülfidik bağların uzunluğunun yanı sıra halkalı sülfid, sarkık hızlandırıcı artıklar, komşu çapraz bağlar malzemenin ısıl kararlığını ve aşağıda anlatılacak olan geri dönüş kararlılığını etkileyen diğer etkenlerdir.

Bir kauçuğun pişme hızı hızlandırıcının tipine bağlı olarak değiştirilebildiği gibi hızlandırıcı/kükürt oranına bağlı olarak da kontrol edilebilmektedir. Hızlandırıcı/kükürt oranına bağlı olarak pişirme sistemleri; konvansiyonel pişirme sistemi (KOV), yarı etkin pişirme sistemi (YEV) ve etkin pişirme sistemi (EV) olarak sınıflandırılmaktadır. Konvansiyonel pişirme sisteminde hızlandırıcı/ kükürt oranı yaklaşık 0,5 /3,5 (phr/phr) iken yarı etkin pişirme sisteminde 2/2 (phr/phr), etkin pişirme sisteminde ise 3,5/0,5 (phr/phr) oranındadır. Tez kapsamında yukarıda belirtilen hızlandırıcılar ve bu üç pişirme sistemi kullanılarak hazırlanan karışımlar mekanik, termo-mekanik ve yaşlanma özellikleri açışından incelenip, hızlandırıcı türünün ve pişirme sisteminin bu özelliklere olan etkileri ortaya konmuştur.

NR/CR esaslı karışımlarda hızlandırıcı türü ve pişirme sisteminin mekanik, termo-mekanik ve yaşlanma özellikleri üzerindeki etkiyi araştırmak için, reçetedeki tüm diğer bileşenlerin miktarı sabit tutularak, sadece hızlandırıcı/kükürt oranı değiştirilerek ve beş farklı hızlandırıcı kullanılarak on beş farklı karışım hazırlanmıştır. Daha sonra hareketli kalıp reometresi kullanılarak süre ve sıcaklık optimizasyonu yapıldıktan sonra tüm karışımların reolojik özellikleri incelenmiştir.

Elde edilen sonuçlara göre TMTD, MBT, DPG sistemleri kendi içinde karşılaştırıldığında çok hızlı sınıfında olan TMTD ile pişmenin tamamlanması için geçen süre (t_{90}) değeri KOV (konvansiyonel vulkanizasyon) sistemde 1,46 dk. iken bu değer orta hızlı MBT de 2,96 dk. 'ye çıkmıştır, yavaş hızlandırıcı DPG de ise daha da artarak 3,65 dk. olmuştur. Pişmede M_H değerine ulaşıldıktan sonra tüm sistemlerde tork değerinde tekrar bir düşüş yani reversiyon olarak isimlendirilen geri dönüş gözlenmiştir. Polisülfidik bağların mono sülfidik bağlara olan dönüşümünden ve zincir kesilmesinden kaynaklanan bu düşüşün sadece hızlandırıcının sınıfı ile değil vulkanizasyon sistemine bağlı olarak da değiştiği görülmüştür. En düşük geri dönüş (reversiyon) TMTD hızlandırıcısı kullanılarak konvansiyonel sistemle elde edilen elastomerde gözlenmiştir. Hızlandırıcının vulkanizasyon etkinliği yada hızı azaldıkça reversiyon reaksiyonlarının arttığı görülmüştür. Reversiyon reaksiyonları TMTD < MBT < DPG sıralamasına göre artma gözlemlenmiştir. Bu sonuç kür reaksiyonlarının hızının azalmasıyla geri dönme reaksiyonlarının artma eğiliminde olduğunu göstermektedir. ZDBC ve DETU hızlı sınıftan birer hızlandırıcı olmasına rağmen NR/CR karışımlarının vulkanizasyonunda TMTD kadar düzenli ve tek basamakta bir çapraz bağlanma kinetiği vermediği görüşmüştür. Konvansiyonel sistemde kükürt oranının yüksek hızlandırıcı oranının en düşük düzeyde olmasından ötürü hızlandırıcı olarak ZDBC ve DETU homojen bir çapraz bağlanma veya ağ yapısı oluşturma eğiliminde olmadığı tespit edilmiştir. DETU ile pişmenin tamamlanması için geçen süre (t_{90}) değeri 5,77 dakikadır. ZDBC de kürleşme 2 basamaklı olduğu için alet tarafından belirlenen 1.85 t_{90} değeri sanal bir değerdir. Düşük ve gecikmiş çapraz bağlama özelliği nedeniyle konvansiyonel sistemde ZDBC ve DETU hızlandırıcıların NR/CR karışımının vulkanizasyonunda tek başına kullanılabilecek uygun bir hızlandırıcı sistemi olmadığı sonucunda varılmıştır. Daha sonra açıklanacağı gibi hızlandırıcı / kükürt oranının artmasıyla yani yarı ektin vulkanizasyon (YEV) sistemine geçilmesi durumunda ZDBC ve DETU, TMDT ye alternatif olarak düşünülebilecek bir hızlandırıcı sistemi olabileceği görülmüştür.

Tüm hızlandırıcılar için yarı etkin vulkanizasyonda t_{90} değeri konvansiyonel sistemden daha düşük olduğu görülmüştür. Bu durum pişme süresi açısından bir avantaj olarak görünse de YEV sisteminde M_H değerine ulaştıktan sonra çok kısa süre geri dönüş reaksiyonları başlamaktadır. Bu durum özellikle ısıyı içinde uzun süre tutabilen büyük parçaların pişirilmesinde bir dezavantajdır. Hızlandırıcının vulkanizasyon etkinliğinin azalmasıyla yani TMDT den MBT ve MBT den DPG ye geçildiğinde reversiyon reaksiyonları konvansiyonel sistemde olduğu gibi giderek artmıştır.

Geri dönüş reaksiyonları etkin vulkanizasyon sisteminde de görülmüştür ancak TMDT ve DPG için oldukça düşüktür. En yüksek düşüş yavaş hızlandırıcı DPG sisteminde gözlenmiştir.

Kür eğrileri genel olarak incelendiğinde en düşük M_H ve Δ tork değeri etkin vulkanizasyon sisteminde gözlenmiştir. Bu sonuç etkin vulkanizasyon ile kür edilmiş sistemlerin en düşük jelleşme (Δ Tork) oranına sahip olduğunun bir göstergesidir (DETU sistemi hariç). DETU ile yapılan vulkanizasyon çalışmalarında diğer sistemlerde olduğu gibi bir sistematik davranış gözlenememiştir.

Kür Hızı İndeksi (CRI) değeri bir kauçuk hamurunun vulkanize olmamış formdan vulkanize olmuş forma dönüşmesinin hızının bir ölçüsüdür. CRI değerinin artması sistemin daha hızlı piştiğini göstermektedir. Daha önce belirtildiği gibi TMTD, ZDBC ve DETU çok hızlı MBT orta hızlı, DPG ise yavaş hızlandırıcı sınıfındadır.

KOV, YEV ve EV sistemlerinde TMTD vulkanizasyonu en hızlı gerçekleştiren hızlandırıcıdır. YEV ve EV sistemleri için beklendiği gibi MBT nin etkinliği TMTD den daha düşüktür, DPG ise MBT den daha düşük etkinliğe sahiptir. Çok hızlı sınıftan olan ZDBC'nin NR/CR karışımı için vulkanizasyon hızı KOV ve YEV sistemlerinde TMDT kadar yüksek olduğu görülmüştür. DETU her iki sistemde de ZDBC den daha yavaş kalmıştır. Bu iki sistem için hızlı sınıftan üç hızlandırıcı kendi içinde karşılaştırıldığına TMTD>ZDBC>DETU etkinlik sırasını izlediği tespit edilmiştir.

Etkin vulkanizasyon sisteminde yani hızlandırıcını/kükürt oranının 3,5/0,5 olduğu durumda TMTD, MBT ve DPG için etkinlik açısından çok önemli bir bir fark gözlenmemiştir. Bu sonuç belirli bir hızlandırıcı oranını üzerinde bu üç hızlandırıcı için bir seçicilik olmadığını göstermiştir. Bununla birlikte ZDBC ve DETU için hızlandırıcı oranı yine yüksek olmasına rağmen kür hızı indeksi değerlerinin diğer üç sistemden neredeyse 10 kat düşük olması ve bu değerlerin KOV ve YEV daki değerinden de 8-10 kat düşük kür hızı indeksi ile oldukça farklı bir davranış sergilemiştir. Bu sonuçlar bir hızlandırıcının tüm kauçuk sistemleri için her zaman belirli bir hız sınıfı altında değerlendirilemeyeceğini hızlandırıcının yanında kullanılan kükürt oranına bağlı olarak hızlı sınıftan bir hızlandırıcının çok yavaş bir hızlandırıcı sınıfına düşebileceğini göstermiştir.

Bu tezin hedeflerinden biriside hızlandırıcı olarak kullanılan kimyasalların elastomerlerin ağ yapısı karakteristiği üzerindeki etkisinin incelenmesidir. Tez kapsamında ağ yapısının incelenmesi için protonların T_2 (spin-spin) durulma süresinden yararlanılmıştır. Sırasıyla pişmemiş ve yaşlandırılmamış örneklere Spin-Eko puls programı uygulanarak sönüm parametreleri Hahn-Echo- sönüm prensibine uygun olarak ve OriginLab yazılımı kullanılarak Hahn-Echo eşitliğine uydurulmuştur. Buradan q değeri elde edilmiş ve çapraz bağlar arasındaki molekül kütlesi (Mc) hesaplanmıştır. Örneklerin yoğünlğğğ göz önüne alınarak çapraz bağ yoğunluğu (XLD) da hesaplanmıştır.

Puls-NMR çalışmaları sonunda elastomer sistemlerinin hazırlanmasında kullanılan hızlandırıcının vulkanizasyon etkinliği azaldıkça (TMTD>MBT>DPG) çapraz bağlar arasındaki molekül ağırlığının arttığı görülmüştür. Çapraz bağlayıcı sistem ne kadar hızlı ise çapraz bağlanmaların sayısı (XLD) o ölçüde artmaktadır.

Vulkanizasyon etkinliği aynı olan TMTD, ZDBC ve DETU kendi içinde karşılaştırıldığında hem konvansiyonel hem yarı etkin hem de etkin sistem için ZDBC ve DETU kullanılan elastomerlerin çapraz bağ yoğunlukları TMTD den daha düşük, Mc değerleri daha büyüktür. ZDBC ile DETU kendi içinde karşılaştırıldığında ise etkin ve yarı etkin sistemlerde DETU'nun Mc değeri ZDBC'den daha küçüktür. Bu iki sistem için çapraz bağlanma etkinliğinin TMTD > DETU > ZDBC sırasını izlediği bulunmuştur. Konvansiyonel sistemde ise DETU ve ZDBC nin Mc değerleri birbirine oldukça yakındır. Hatta diğer iki sistemden farklı olarak DETU'nun çapraz bağlar arasındaki molekül ağırlığı ZDBC 'den daha fazladır. Konvansiyonel sistemde yukarıda açıklandığı gibi MBT ile DPG arasındaki değişimin ve DETU ve ZDBC arasındaki değişimin diğer sistemlerden farklı olmasının en önemli sebebi konvansiyonel sistemin doğasından kaynaklanabileceği düşünülmüştür. Bilindiği gibi konvansiyonel sistemde kükürt /hızlandırıcı oranı 3,5/0,5 dir. Yüksek kükürt oranı çapraz bağlanmaların hızını ve çapraz bağlanma reaksiyonlarının sayısını arttırırken aynı zamanda mono, di, polisülfidik ve halkalı reaksiyonlarının dağılımını ve bu reaksiyonların kontrolsüz olarak oluşma olasılığının da artmasına yol açar. Bu hızlı de gelişigüzel reaksiyonlar zinciri konvansiyonel sistemdeki sıralamanın diğer sistemlere göre daha karmaşık bir seyir izlemesine yol açmış olabilir.

Hazırlanan tüm karışımların Evrensel Test Cihazı ile mekanik özellikleri incelenmiştir. Elde edilen ilk sonuçlar NR/CR elastomerlerinin mekanik özelliklerinin elastomer sistemin hazırlanmasında kullanılan hızlandırıcının vulkanizasyon etkinliğine yani çok hızlı, orta hızlı veya yavaş olmasına bağlı olarak değiştiği görülmüştür. Ayrıca vulkanizasyon etkinliği aynı olmasına rağmen sınıfının değişmesi de mekanik özelliklere etki ettiği görülmüştür.

Örneğin endüstriyel uygulamalara en çok tercih edilen Konvansiyonel vulkanizasyon sisteminde vulkanizasyon etkinliği artıkça (TMTD>MBT>DPG) kopmadaki uzama değerinin azaldığı, kopmadaki kuvvet değerinin arttığı görülmüştür. Vulkanizasyon etkinliği aynı olan TMTD, ZDBC ve DETU kendi içinde karşılaştırıldığında ZDBC ve DETU kullanılan sistemlerin mekanik özellikler açısından TMTD kullanılan sistemlerden daha zayıf olduğu görülmüştür. ZDBC ve DETU mekanik özellikler açısından birbirine çok yakın davranış sergilemiştir. Bunun en önemli sebebi çapraz bağ yoğunluklarının birbirine yakın olmalarından kaynaklanabilir.

Bir elastomer sistemin çapraz bağ yoğunluğunun değişimi fiziksel özellik olarak kendini öncelikle kopmadaki uzama özelliği üzerinde hissettirir. Konvansiyonel ve yarı etkin sistem için NMR çalışmalarında elde edilen sonuçlara paralel sonuçlar elde edilmiştir. Etkin sistemde ise daha yüksek çapraz bağ yoğunluğuna sahip olmasına rağmen TMTD nin % uzama değeri hem MBT hem de DPG nin % uzama değerinden daha yüksek bulunmuştur. Bunun sebebi mekanik özelliklerden, kopmadaki uzamanın ağ yapısının çapraz bağ yoğunluğu kadar çapraz bağlanmalarının dağılımı ile de yakından ilişkili olmasıdır. Örneğin TMTD kullanıldığında monosulfidik bağlanmaların yanı sıra sistemde polisülfidik bağlanmalarında oluşturduğu bilinmektedir. Polisülfidik bağlanmaların varlığı TMDT sistemi için kopmadaki kuvvet değerinin beklenenden daha büyük olmasına yol açmış olabilir.

Hazırlanan karışımların ağ yapılarını ve buna bağlı olarak durulma davranışlarını incelemek için yeni bir yöntem olan Sıcaklık Taramalı Gerilim Durulma analiz yöntemi kullanılmıştır. Sıcaklığa karşı normalize kuvvet grafikleri elde edilmiş ve başlangıçtaki kuvvetin %10, %50 ve %90 kayıp yaşandığı sıcaklıklarının yanı sıra başlangıçtaki gerilim ve elastik özelliğin bir göstergesi olan TSSR indeks miktarları belirlenmiştir.

Tüm pişirme sistemlerinde gerilim düşüşü TMTD>MBT>DPG sırasını izlediği tespit edilmiştir. ZDBC ve DETU hızlandırıcı içeren örneklerin davranışında diğer özelliklerinde olduğu gibi farklılık olduğu gözlemlenmiştir. Bu karışımlarda diğerlerinden farklı olarak 75-125°C aralığında bir platu bölgesi görünmektedir. Bunun sebebi diğer örnekler NR ve CR için en yüksek sıcaklık dayanımı olan ortalama 110°C sonra bozulmaya başlarken bu örneklerde yapılarında tepkimeye girmeyen serbest kükürtün bir bölümünün sıcaklıkla birlikte çapraz bağ yapmaya başlaması ve gerilim durulmasını belli oranda dengelemesi olabilir. Farklı sistemler karşılaştırdıklarında, belirgin bir düzene rastlanmamıştır. Bunun sebebi de stress durulma davranışının sadece çapraz bağ yoğunluğu ile bağlı olmadığıdır. Durulma davranışının çapraz bağların uzunluğu (türü) ayrıca sıcaklık ve gerilimin etkisiyle oluşabilen ikincil bağ oluşumu ve bozulmasıyla ilişkili olmasıdır. Başlangıçtaki kuvvet değerleri incelendiğinde bu değerin çapraz bağ yoğunluğuyla ilişkili olduğu görülmüştür. XLD artıkça σ_0 değerinin de artığı gözlemlenmiştir.

Hazırlanan tüm kauçuk örnekleri deneysel çalışmaların ikinci aşamasında hızlandırılmış UV yaşlandırmasına tabi tutulmuştur. Örnekler toplamda 8 gün hızlandırılmış iklimlendirme cihazında yaşlanmaya bırakıldıktan sonra, daha önce belirtilen yaşlanmamış örnekler için yapılan analizler aynı koşullarda yaşlandırılmış örnekler için tekrarlanmıştır.

Mekanik analizler sonucunda sistemler arasındaki karşılaştırmada yarı etkin sistemin en kötü yaşlanma performansını gösterdiği görülmüştür. KOV ve EV sistemleri karşılaştırdıklarında daha düşük miktarda kükürt içeren EV sistemi ile pişirilen örneklerin daha az yaşlandıkları tespit edilmiştir. Hızlandırıcıların içerisinde MBT nin çok iyi performans gösterdiği ayrıca DETU'nun en az yaşlanma özelliği ile TMTD ye alternatif oluşturabileceği gözlemlenmiştir.

Yaşlandırılmış örneklerin çapraz bağ yoğunlukları incelendiğinde, beklendiği üzere yaşlanma sonucunda XLD artığı görülmüştür. Yine ZDBC ve DETU değerlendirmenin dışında bırakılacak olursa hızlandırıcıların pişirme etkinliği azaldıkça yaşlanma sonucunda XLD artışının da azaldığı tespit edilmiştir. Sistemler içerisinde karşılaştırmada daha az kükürt eşittir daha az çapraz bağ artışı kuralının geçerli olduğu tespit edilmiştir.

Yaşlanma sonunda durulma davranışı değişimi incelendiğinde, yaşlanma sonucunda tüm örneklerin gerilim düşüşünün daha yüksek sıcaklıklara kaydığı görülmüştür. TSSR indeks açısından yaşlanmamış örneklerdeki gibi CV>SEV>EV düzeni geçerlidir ve yaşlanma tüm örneklerin TSSR indeksini artmasına sebep olmuştur ki bunun çapraz bağların yoğunluk artışı ve polisulfidik bağların daha az esnek olan mono ve disulfidik bağlara dönüşmesi olduğu düşünülmektedir. TSSR eğrileri yaşlandırma öncesi ve sonrası detaylı bir şekilde incelendiğinde, gerilim durulma davranışının özellikle NR-CR karışımları için beklenen parametreler dışında, gerilim etkili kristallenme ve sıcaklık etkili çapraz bağ türü değişimi gibi faktörlerede bağlı olduğu için basit ve düzenli bir davranış değişimi sergilemesini mümkün olmadığı kanısına varılmıştır.

Bu tez kapsamında yapılan tüm deneysel çalışmalar sonucunda NR/CR karışımları için, son kullanım amacı da göz önüne alınarak pişirme sistemi olarak KOV veya EV sistemlerden birini pişirme sistemi olarak seçmenin doğru seçim olacağı tespit edilmiştir. Yaşlanmanın önemli olabileceği kullanımlarda EV sistemi birinci tercih olmalıdır. Tüm bu sonuçlar ışığında NR/CR karışımı için hızlandırıcı seçimindeyse MBT gibi orta hızlı bir hızlandırıcıyı kullanmak mekanik, termo-mekanik ve yaşlanma açısından avantaj sağlayacağı tespit edilmiştir.

Anahtar kelimeler: Doğal kauçuk, kloroprenkauçuk, hızlandırılmış yaşlandırma, pulse NMR, Sıcaklık Taramalı Gelilim Durulması

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SYMBOLS & ABBREVIATIONS

Symbols

B	Magnetic field
C	Backbone units per Kuhn-segment
L	length
Mc	Averaged molecular mass between crosslinks
MH	Maximum torque
ML	Minimum torque
MRU	Average molar mass of one monomeric units
N	Backbone bonds per monomeric unite
q	Motion factor
R	Universal gas constant
t 90	Cure time at 90% cure
T1	Spin-lattice relaxation time
T2	Spin-spin relaxation time
ts2	Scorch time till two torque unit rise above the minimum
ε	Strain
σ	Stress
λ	Strain ratio
τ	Relaxation time

Abbreviations

CR	Chloroprene rubber
CSM	Chlorosulphonated polyethylene
SEV	Semi-efficient vulcanization
CV	Conventional vulcanization
DOTG	Di-ortho-tolyguanidine
DPG	Diphenylguanidine
DTDM	Dithiodimorpholine
EPDM	Ethylene propylene Diene monomer rubber
EV	Efficient vulcanization
IIR	Isobutylene isoprene copolymer
IR	Polyisoprene
MBT	2-mercaptobenzothiazole
MBTS	2-mercaptobenzothiazole disulfide
NBR	Nitrile butadiene rubber
NR	Natural rubber
phr	Part per hundred rubber
PPD	P-Phenylenediamine
PVI	Pre-vulcanisation inhibitor
SBR	Styrene butadiene rubber
TMQ	Trimethyl-dihydroquinolines
TMTD	Tetramethylthiuram disulfide
VGC	Viscosity-Gravity Constant
ZMBT	2-Mercaptobenzothiazole

OTBG	Orthotolybiguanidine
TETD	tetraethyl thiuram disulfide
DMPTD	dimethyl diphenyl thiuram disulfide
TMTM	Tetramethyl thiuram monosulfide
HAF	High-abrasion furnace
MDR	Moving die rheometer
NMR	Nuclear magnetic resonance
TSSR	Temperature scanning stress relaxation
UV	Ultra violet
ODR	Oscillating die rheometer
CRI	Cure Rate Index
XLD	Crosslink density
FID	Free induction decay

1. INTRODUCTION

Elastomers better known as rubbers play a significant role in our lives since their introduction in 1839 by Charles Goodyear. Although the principles of sulfur vulcanization have remained more and less the same, chemicals have improved the efficiency of the process, quality and durability of the vulcanizates ever since. After their first commercial application in 20s, organic accelerators became one of the main components of every elastomer recipe. Application of accelerators have reduced the amount of the sulfur used to reach an optimum crosslink density. Reduction of the sulfur amount has improved processability of elastomers by reducing cure time and probability of scorch. It also helped to improve mechanical and aging properties of vulcanizates. Mercapto benzo thiazole (MBT) was the first commercially used accelerator but its success brought about dozens of different accelerators with different properties which can be applied alone or alongside other accelerator to add a variety of different properties to rubber vulcanizates. In the following years, some of these accelerators have been used not only to accelerate vulcanization but also to act as sulfur donners in recipes reducing or even eliminating use of sulfur in its pure mode. Since these organic accelerators have different chemical structure and properties, the all have different effects on every property of the vulcanizates, from thermal, mechanical and aging properties to network structure and cure kineties. No need to say that these effects are also related mainly to the elastomer or elastomers used in recipe and other components.

Since accelerators interact with sulfur in sulfur curing systems to facilitate vulcanization, the relative amount of these components, is so important that is regarded as vulcanization system. There are three sulfur vulcanization systems considering relative amount of sulfur and accelerator present in the recipe. Conventional vulcanization system, semi-efficient vulcanization system and efficient vulcanization system.

In Conventional Vulcanization (CV) system, sulfur ratio is higher than the accelerator, leading to the formation of crosslinks, which are predominantly polysulfidic. Although CV cured vulcanizates show better fatigue and tear resistance, their ageing characteristics are not as good as efficient vulcanization (EV) system in which accelerator amount exceeds sulfur amount. Consequently, the use of a semi-efficient (semi-EV) vulcanization system with more and less the equal amount of sulfur and accelerator was found to be more suitable in many cases.

So accelerator type and accelerator to sulfur ratio plays a determinative role in network structure of the sulfur vulcanizates, which in turn determines crosslinking density, mechanical properties and aging characteristics of the final products. To our knowledge, effects of accelerator type and vulcanization system on network structure have never been investigated in detail and correlations between rheological and stress relaxation behaviors and crosslink density and type has never been revealed for sulfur vulcanizates. This thesis dedicated to reveal these inter relations since this information can help researchers, chemists and engineers to choose the proper accelerator and vulcanization system concerning their desired properties of final elastomeric product.

To reach this goal at the first phase of experimental works a series of NR/CR compounds have been compounded differing only in accelerator types and accelerator to sulfur ratio. Then these compounds have been cure according to cure curve data and then the vulcanizates have been tested for their mechanical properties as well as crosslink density and stress relaxation behavior. At the second phase of research, the vulcanizates have been exposed to accelerated weathering conditions to investigate weathering effect on each vulcanizate. At the end, comparisons have been made and relations between accelerator type and vulcanization system on one hand and crosslink density, mechanical properties and stress relaxation character of the vulcanizates have been established.

2. GENERAL INFORMATION

2.1. Rubber Components

2.1.1. Natural Rubber

Natural rubber consists of 99% cis-1,4-polyisoprene and mainly produced from the latex of the Hevea brasiliensis tree. Because of NR's stereoregularity, its polymer chains can spontaneously pack together as crystallites. The rate of crystallization of natural rubber reaches maximum values when stored at – 25°C. NR also crystallizes upon straining. This strain-induced crystallization increases cut grow resistance at severe deformations.

History of natural rubber application by humankind dates back to 1300–300 BC during the Olmec civilization of America.

Usage of natural rubber continued among the Mayans, the Incas, and the Aztecs until the Spanish destruction of the Central and South American civilizations. Natural rubber was mainly used to make balls. Ball game was considered an important religious and political event, since victory or defeat was used to determine the outcome of wars.

A Spanish priest, P. Martyre d'Anghiera, attached to the invading army, first wrote about rubber in his book '*De Orbo Novo*', which was published in 1530. Further literature was published, but the useful application of rubber remained unknown among Europeans for nearly 200 years. A breakthrough on rubber came from French scientists; F. Fresneau (1703–1770) was an agricultural scientist working at the colonial office in French Guiana. While travelling in Guiana and the Amazon in search of economically useful plants, he became interested in rubber-producing trees on which he prepared a report and gave a lecture at French Academy of Science in Paris. This was the first scientific report on rubber.

In England, the chemist Joseph Priestley, noticed that pencil marks could be erased (rubbed out) by rubber. This caused Priestly to use the word 'rubber' to refer to this material.

In the nineteenth century two Englishmen, Charles Macintosh (1766–1843), an entrepreneur and Thomas Hancock (1786–1865), an engineer, began the industrialization of rubber products Macintosh applied rubber solution to a cloth and found that it became highly water-resistant. In cooperation with Hancock, he began to manufacture raincoats using the rubberized cloth

The problem with this new material was that, at low temperatures, it became hard and lost elasticity, while at high temperatures it became too soft to retain its original shape.

In 1839, Charles Goodyear developed the process of vulcanization [1]. This consisted of a cross-linking reaction of rubber molecules with Sulfur to give a three-dimensional and stable network structure. As a result, natural rubber became an industrially important resource and a strategically indispensable material during times of war. However, the mechanical details of the reaction have only recently been investigated and a full explanation of the process has not yet appeared. Figure 2.1 represents natural and commercial form of the natural rubber.

Fig. 2.1. Hevea tree during natural rubber harvest (left) and commercialized natural rubber sample (right)

Rubber has always been a strategic resource especially at war times therefore numerous attempts have been made to find a replacement for Hevea tree and American scientists continue to work on *Parthenium argentatum* (Guayule) [2-4], a shrub found in Mexican deserts. This plant was cultivated in the United States during the Second World War, when synthetic rubbers underwent rapid development due to the scarcity of natural rubber. Russian scientists cultivated *Taraxacum kok-saghyz* (Russian dandelion rubber) during the 1930s and 1940s. Despite these efforts, *Hevea brasiliensis* remained as the best source of natural rubber in the world.

Currently, Thailand, Indonesia, Malaysia, India, China, Sri Lanka and Vietnam are the main natural rubber producing countries. With the ever-growing demand for natural rubber products and global increase of its price, Cambodia, Laos, Bangladesh and some African countries may also become major producers.

The application of techniques such as genome analysis is likely to become significant in the scientific study of natural rubber, particularly among biochemists and agriculturalists [5, 6]. These studies will open new horizons on understanding and applications of this fabulous natural product.

No need to mention that in recent years, increase of environmental concerns and natural rubber global price have increased attempts to reclaim and recycle vulcanized natural rubber.

2.1.2. Synthetic Rubbers

After the successful application of natural rubber and its commercial success and together with development of other synthetic polymers, efforts have been made to develop synthetic rubbers. The earliest recorded accounts of the production of synthetic rubbers by polymerization refer to isoprene, a substance that is closely related to the repeating unit in the molecule of natural rubber.

The first patent to be granted for the manufacture of synthetic rubber was to for the production of a rubbery Matthews and Strange in 1910 get the first patent for synthetic rubber. This important discovery was made accidentally in while trying to dry isoprene by means of sodium metal. A similar discovery was made almost simultaneously in Germany by Harries and the Bayer Company.

In 1910 Russians, synthetized polybutadiene. Some twenty years later German scientists began commercial production of styrene butadiene copolymer. By the start of the Second World War, huge R & D projects started which aimed to develop strategically important rubber. Styrene butadiene rubber was modified in USA and manufactured on a large scale with the name of Government Rubber-Styrene (GR-S). This rubber, which is known as

SBR today, is one of the major and commonly used materials in the rubber industry. Styrene butadiene rubber is undoubtedly the most important synthetic rubber in terms of consumption and production amount. Other synthetic rubbers, which were produced during Second World War, also have a significant place in today’s market.

Julius Aloysius Nieuwland a priest and a chemistry professor of Notre Dame University synthesized chloroprene by passing divinyl acetylene over sulfur dichloride. DuPont purchased the patent and its scientists sensitized a rubber using this chemcal which named as Duprene [7], in 1931. This name changed to Neoprene. Polychloroprene, CR or chloroprene rubber are the names used alongside with Neoprene, which is the most commonly used name for this product.

Nitrile rubber, NBR or nitrile butadiene rubber prodused in 1934 in Germany with the name of Buna-N as an oil resistant elastomer. This name changed to Perbunan later on.

Butyl rubber, IIR or isobutylene isoprene copolymer was developed in the 1940s in USA as an air impermeable elastomer.

Hypalon (CSM, chlorosulphonated polyethylene) and Viton (FKM, fluoroelastomer) which were developed in 1950s and ethylene propylene terpolymer rubber (EPDM) which was developed in the 1960s are other significantly used elastomers in modern rubber industry. Commercially successful synthetic analogue of natural rubber did not appear until 1960s. Shell company commercialized synthetic analogue of NR as ‘Shell Isoprene Rubber’ and shortly after Goodyear introduced Natsyn. It is chemically known as polyisoprene (IR), and it could not in any way displaced or replace natural rubber [8, 9].

2.1.3 Chloroprene Rubber

Chloroprene is a product of emulsion polymerization of 2-chloro-1,3-butadiene, mostly 88 to 92% trans and glass transition of about - 50 °C. Chloroprene is available in several grades in order to aid compounding and to emphasize desired properties, such as reduction of crystallization rate in the vulcanizate. CR is partly oil and weather resistance. Chloroprene rubber’s oil resistance considered moderate. The electron-withdrawing character of chlorine atom present in CR structure, deactivates the double bond towards oxygen and ozone attack. This effect also imparts polarity to the elastomer, making it resistant to swelling by hydrocarbons. CR has superior weatherability, heat resistance, flame resistance, and adhesion to polar substrates, such as metals compared to other commercial rubbers. CR also has lower permeability to air and water vapor, which makes it a preferred economic choice for multi-purpose rubber compounding.

CR and NR has similar dynamic mechanical characteristics, such as good mechanical strength. CR's partial flame retardant character will give it the ability to extinguish itself when the source of fire has been removed. In the same case rubbers like NR, EPDM, and SBR, will continue to burn.

CR's upper heat aging resistance temperature limits can be raised by special formulation and compounding techniques. At the low end of the temperature range, Chloroprene rubber shows a degree of stiffening at around -18 °C, and it becomes brittle around -40 °C. Resistance of CR to dilute acids and bases is better than that of NR or SBR, while cost is somewhat higher. It is good to mention that certain grades of CR are produced specifically for the adhesives marketplace.

Fig. 2.2. Commercial form of chloroprene rubber also referred to as neoprene

2.1.4. Carbon Black as a Filler

Fillers that are used in rubber industry can be categorized in different ways. According to their color, and then we have two main groups

1. Black fillers (e.g. carbon black)

2. Non-black fillers, sometimes referred to as white fillers (e.g. calcium carbonate)

In addition, they can be categorized according to their final effect on mechanical properties of elastomers. According to their effects fillers grouped as

1. Reinforcing fillers (e.g. N330 carbon black)
2. Semi-reinforcing fillers (e.g. Microcal ET calcium silicate)
3. Non reinforcing fillers (e.g. calcium carbonate)

It is good to mention that many fillers can lay in different categories as their size varies. Smaller size fillers usually show better reinforcing effect.

Fillers also can be categorized do to their chemical structure, nature and synthesis methods. Then they would categorized as

1. Natural fillers (kaolin)
2. Synthetic and Precipitated fillers (e.g. calcium carbonate)
3. Pyrogenic fillers (e.g. carbon black types)
4. Surface Modified fillers (e.g. silanized silica)

Specific gravity, particle size and surface area of fillers are the most important factors that are effecting final properties of the elastomeric products. Specific gravity of the fillers play an important role in the product weight and therefore its price.

Particle size and distribution is the most important factor in reinforcing ability of the filler. Filler size is in the range of 1-5000 nm. Reinforcing fillers range from 1 to 100 nm. Surface area of the filler particles increases with the decrease in particle size improving the reinforcing ability of the fillers.

The fact that carbon black can be added in significant amounts into the rubber formulations not just for making a cheaper product but also reinforce it has been discovered in the beginning of twentieth century. Lampblack, which is a product of smoky oil flames, collected and sold as carbon black in the early days of carbon black production. The next historical step was to burn natural gas against iron channels, then scrape off the carbon to produce a highly reinforcing material called channel black [10].

In 1923 Frank and Marckwald prepared identical products using both German (lampblack) and American (oilblack) carbon blacks and found that their physical properties were significantly different with the former giving a more elastic product and the latter a much tougher material. Detailed studies have proved that by changing the production process and starting materials, the produce different types of carbon black can add variety of important qualities to the final rubber vulcanizate.

The important parameters, which dominate the final product properties, include

1. Carbon black type and Particle size
2. The amount added to the rubber
3. Dispersion within the mix.

The American Society for Testing and Materials (ASTM) specifies generic codes for these grades (ASTM D 1765 [11]. Rubber grade carbon blacks are classified using a four-character designation.

The first character can be either an "N" or an "S." The assigned letter designates the effect on the cure rate of a typical rubber compound containing the black. The cure rate may be normal-"N" or slow-"S." The vast majority of all carbon blacks assigned an ASTM designation are "N" type, typical of furnace technology. The "S" designation is used to define channel blacks or modified furnace blacks where the cure rate has been reduced.

The second character is a single digit that defines the average surface area as measured by nitrogen surface area (ASTM D6556 [12]). Ten groups have been defined to characterize the range of the surface areas [13]. The groups are defined in Table 2.1.

Table 2.1. Carbon Black Classification (based on ASTM D 6556).

Group No.	Average Nitrogen Surface Area (m^2/g)
0	>150
1	121 to 150
2	100 to 120
3	70 to 99
4	50 to 69
5	40 to 49
6	33 to 39
7	21 to 32
8	11 to 20
9	0 to 10

The third and fourth characters are arbitrarily assigned by the chairman of Subcommittee D24.41, if the requestor has not asked for a specific designation.

A decrease in carbon black particle size (increase in overall surface area to volume ratio) increases the tensile strength of the cured vulcanizate.

Carbon black size and type can also effect hysteresis, abrasion, electrical conductivity and many other properties of elastomers [14-16]. For example, Chang Kook Hong et al. have studied the effect of the particle size and structure of carbon blacks on the abrasion of filled natural rubber, styrene–butadiene rubber and polybutadiene compounds elastomer compounds. The results shows that the abrasion rates decrease with increasing surface area and developing structure of carbon blacks. The result also indicates that the abrasion rate is proportional to a power of the applied frictional work input.

As a powerful ultra violet absorber, carbon black adds a measure of protection against sunlight to the rubber. This protection is especially important for unsaturated elastomers such as Natural rubber and SBR which has very low resistance to weathering.

2.1.5. Oils & Plasticizers

Plasticizer is the general name for oils and other ‘slippery’ materials. At ASTM D1566 [17] they have been defined as ‘a compounding material used to enhance the deformability of a polymeric material’. At low levels they function as to aid the dispersion of fillers in the rubber matrix by reducing viscosity of the uncured compound. They also help to reduce compound cost and hardness. In some cases, they are used to improve low temperature flexibility. They reduce the elasticity of the uncured compound which in turn improves flow in extrusion and molding. The important aspect to be considered using plasticizers is their compatibility with elastomers. Relative polarity is the main factor when it comes to choose the right plasticizer type. The incompatibility can cause separation problem. This problem can show itself as exudation, bloom, volatility or fuming during process. The importance of plasticizer effect on processability of the elastomer and finding non-toxic replacements for them keeps is the driving force of many researches in this filed [18-20]. M da silva et al. aimed to find an alternative natural polymeric plasticizer obtained through polyesterification of rice fatty acid for natural rubber [19] is an example recent studies. They find out this fatty acid increases elongation and decreases tensile strength of natural rubber vulcanizates so it can be used as an alternative non-toxic plasticizer.

Oils are the major plasticizer used in rubber compounding. The oils used in rubber compounding differ from each other in these aspects [13]

1. Degree of aromaticity
2. Average molecular weight
3. Volatility
4. Percent polar compounds
5. Percent asphaltenes
6. Wax content

All oil molecules usually have three types of structures in common. These structures are:

1. Aromatic
2. Naphthenic
3. Paraffinic

Types of oil differ in proportional quantity of each structure. One method to statistically relate to the dominant chemical structure of a petroleum oil is to use ASTM D2501 [21], Viscosity-Gravity Constant (VGC) which is calculated from specific gravity and viscosity. Classification scheme to classify oils has been presented in Table 2.2.

Table 2.2. Classification scheme of oils

Oil Type	VGC
Paraffinic Oil	<0.82
Relatively Naphthenic Oil	0.82 - 0.85
Naphthenic Oil	0.85 - 0.90
Relatively Aromatic Oil	0.90 - 0.95
Aromatic Oil	>0.95

Paraffinic oils have better rebound resilience and lower hysteresis, while aromatics are better for tensile strength and resistance to crack growth.

Viscosity of the oils with similar chemical structure is determined by average molecular weight. Oil viscosity can affect the processability characteristics imparted to a rubber compound. Also, higher viscosity may impart better permanence and aging resistance to vulcanizates.

The oils that contain excessive amount of low-molecular-weight components, show poor aging properties.

Quinoline, thiophene and Phenols are examples of polar compounds present in oils and have been reported in the literature to affect cure behavior of a rubber compound.

In order to improve flame retardation properties of compounds, chlorinated oils might be used.

Liquid plasticizers such as esters (polar liquids) are used for NBR and other oil retardant elastomers. Esters can also improve low temperature flexibility.

Waxes can also be an important characteristic for rubber process oil. Petroleum wax molecules can be very much like other oil molecules except they contain mostly the paraffinic structures and only a small number of naphthenic and aromatic rings. Do to higher crystalline tendency of waxes they are less compatible with rubber at lower temperatures. Wax type and amount can also affect the bloom characteristics of rubber compounds.

2.1.6. Antioxidants, Age Resistors and Antidegradants

Antioxidants are necessary to protect most elastomers' from aging by eliminating free radicals. Many vulcanizates become brittle when they age. The ravages of oxygen, accelerated by heat, can cause aging in more and less all of the elastomer types. Antioxidants are designed to slow down this process and can act as free radical scavengers.

While some antioxidants improve flexibility of the product (antiflex cracking antioxidants) others like Antiozonants such as the p-phenylene diamines, provide sacrificial protection against ozone. This chemical group also has very good antioxidant activity. ASTM D3853 [22] contains standardized symbols for antioxidant chemical names.

Antidegradants are added to a rubber compound to protect the vulcanizate from oxidative attack. An antidegradant can function as an antioxidant and/or an antiozonant. ASTM D4676 [23] classifies these rubber antidegradants into six different classes. These classes are listed here.

1. P-Phenylenediamine (PPDs)

This class of antidegradant is primarily used in tires and in some mechanical rubber goods as an antiozonant to give protection against ozone attack while the rubber is flexing. These chemicals are also used for their antioxidant and antiflex fatigue characteristics that they impart to the compound.

Unfortunately, these additives will impart staining and discoloration characteristics to a rubber compound as well. Different members of this class will impart different degrees of ozone resistance and flex resistance. These PPD compounds bloom to the surface of the rubber article in order to react with ozone and protect the rubber surface. Different types of PPDs have different degrees of chemical reactivity with ozone, different degrees of solubility, and different diffusion rates in the rubber compound. These characteristics determine how much protection a given PPD will impart to a rubber article and whether it will be long-term or short-term protection. Figure 2.3 shows the chemical structure of PPDs.

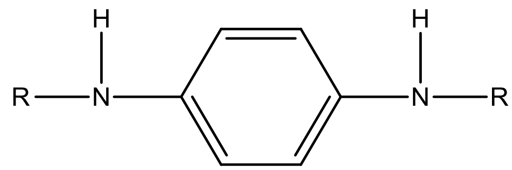

Fig. 2.3. Chemical structure of PPDs. R can be alkyl, aryl, or both

2. Trimethyl-dihydroquinolines (TMQs)

These rubber additives are general-purpose antioxidants used to protect rubber products from atmospheric oxygen attack, especially at higher temperatures. The chemicals in this group are among the most popular antioxidants used in the rubber industry. They are the condensation products from the reaction of aniline and acetone. Polymerization degrees and softening points of the antioxidants of this class can be variable. Figure 2.4 shows chemical structure of a general TMQ type antioxidant.

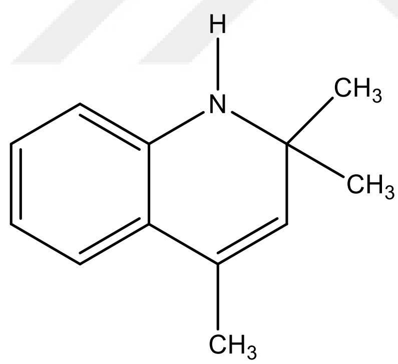

Fig. 2.4. General form of a TMQ type antioxidant

3. Phenolics

Chemicals in this group are used as weaker antioxidants and are relatively nonstaining and nondiscoloring. These antioxidants are used in light colored mechanical goods and in tire white sidewall applications. Chemical structure of this group of antioxidants have been presented in Figure 2.5.

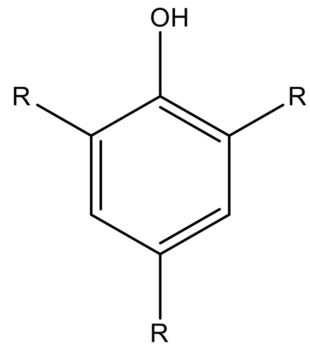

Fig. 2.5. Chemical structure of phenolic type antioxidants

4. Alkylated Diphenylamines

This class is a good representation of substituted amine antioxidants used in rubber compounding and is generally considered moderately staining and discoloring in a compound. Chemicals of this group are very common and effective as radical scavenger [24, 25], due to their special molecular structures and high stoichiometric efficiency. General chemical structure of this group have been represented in Figure 2.6.

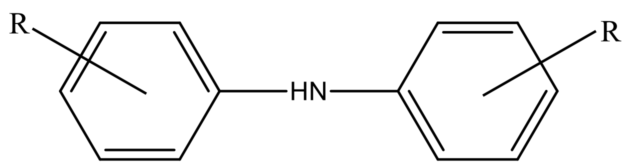

Fig. 2.6 General chemical structure of alkylated diphenylamine antioxidants

5. Aromatic Phosphites

Chemicals in this group used as stablizers for synthetic elastomers and are nonstaining relative to other classes of antioxidants. Figure 2.7 is the representation of their chemical structure.

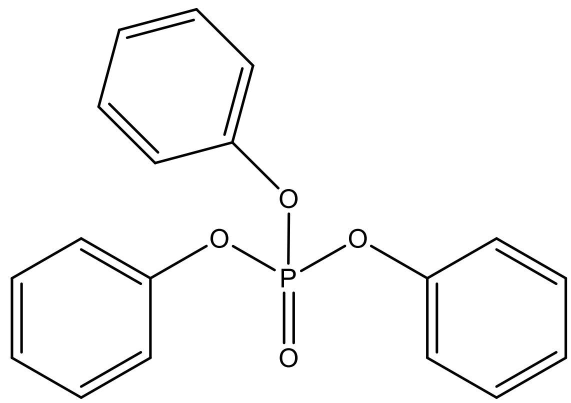

Fig. 2.1. Chemical structure of aromatic phosphite type antioxidants

5. Diphenylamine-Ketone Condensates

This class of rubber antioxidant is generally manufactured as a reaction product of diphenylamine and an alkyl ketone, usually acetone. This class is mainly used as antioxidant especially at high temperature. The chemicals of this group are usually available in liquid form. General chemical structure for this type of chemicals have been presented at Figure 2.8.

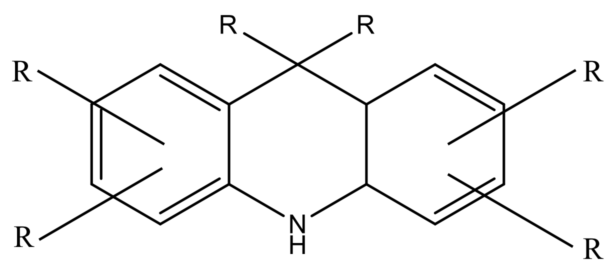

Fig. 2.2. Chemical structure of diphenylamine-ketone condensate type antioxidants

2.1.7. Sulfur Curing Systems

Crosslinking or curing which is a widely used technique to improve polymer properties consists of forming covalent, hydrogen or other bonds between polymer molecules. Charles Goodyear was the first person to introduce the technique in 1839. This sulfur curing technique was first used commercially in, Massachusetts USA, in 1841. The same procedure was used a year later by Thomas Hancock England. Heating natural rubber with sulfur resulted in improved physical properties. The vulcanization time with this method was too long (more than five hours) and the vulcanizates suffered from disadvantages, e.g., ageing properties and mechanical performance. Since then different chemicals and curing techniques have been introduced to reduce the cure time, improve the mechanical, dynamic and thermal properties and reduce the manufacturing coasts.

Initially, vulcanization process consisted of heating sulfur at a concentration of 8 parts per hundred parts of rubber (phr) for 5 h at 140 °C. Vulcanization time had been reduced to three hours by addition of zinc oxide. Introduction of accelerators in concentrations of around 0.5-3.5 phr have reduced times to 1-3 min. As a result, accelerator-free sulfur vulcanization of rubbers is no longer of commercial significance. Ebonite, a hard rubber, which is produced by using of about thirty phr of elemental sulfur, and without accelerator, is an exeption for this general rule. Ebonite has its own application field in modern industry as base material for the manufacture of smoking pipes, pen bodies and parts of musical instruments.

The accelerated sulfur vulcanization of general-purpose diene rubbers (e.g., natural rubber, Styrene butadiene rubber, and butadiene rubber) and other rubbers (e.g., ethylene-propylene-diene terpolymer rubber, butyl rubber, halobutyl rubber, nitrile rubber) in the presence of organic accelerators follows very similar principles and together this sulfur-based vulcanization comprises more than 90% of industrial vulcanization.

During accelerated vulcanization process, monomeric polysulfides of Ac-S_x-Ac type are formed (Ac stands for accelerator). Then these monomeric polysulfides interact with rubber. MBT is formed during this reaction in the case of thiazole type accelerator and natural rubber application. Finally, the rubber polysulfides react, either directly or through an intermediate, to give crosslinks, rubber-S_x-rubber [26]. A reaction scheme have been presented in Figure 2.9.

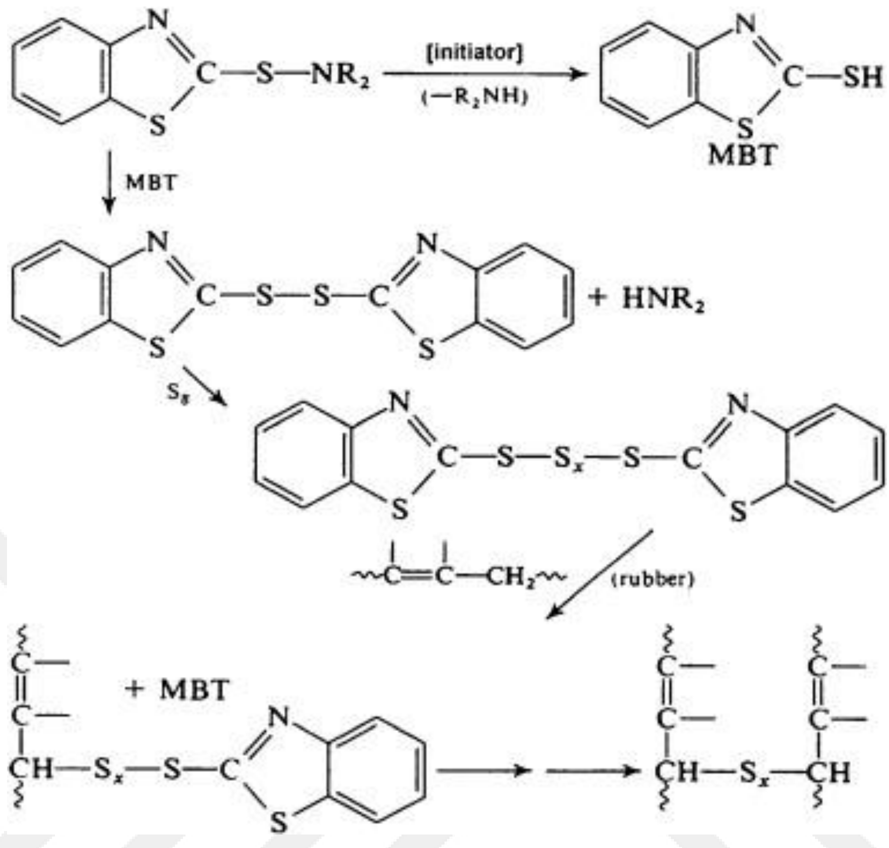

Fig. 2.3. Reaction scheme of accelerated sulfur vulcanization

Over the years three special types of cure systems have been developed. They are:

• Efficient vulcanization (EV) system,

• Semi-efficient vulcanization (SEV) system and

• Conventional vulcanization (CV) system.

EV system is a vulcanization system with low level of sulfur and correspondingly high level of accelerator. It can also be totally sulfur-free. This vulcanization system are used for compounds that are used where extremely high heat and reversion resistance is required. In the conventional curing system, the sulfur dosage is high and correspondingly the accelerator level is low. The conventional vulcanization system considered to provide better flex and dynamic properties. However this system considered to have worse thermal and reversion resistance due to higher amount of sulfur presented in this system. For optimum levels of mechanical and dynamic properties of vulcanisates with intermediate heat, reversion, flex and dynamic properties, the so-called SEV system with an intermediate level of accelerator and sulfur are employed. The levels of accelerator and sulfur in CV, SEV and EV systems are shown in Table 2.3.

Table 2.3. Sulfur & accelerator amounts and their ratio for different vulcanization systems

Vulcanization System	Sulfur (phr)	Accelerator (phr)	Accelerator/Sulfur Ratio
CV	2.0-3.5	1.2-0.4	0.1-0.6
SEV	1.0-1.7	2.4-1.2	0.7-2.5
EV	0.4-0.8	5.0-2.0	2.5-12

Many studies have documented both the advantages (increased age resistance), and the disadvantages (impaired fatigue resistance) of EV and SEV systems [27-35]. All of these studies prove that vulcanization system (accelerator/sulfur ratio) has a significant effect on crosslink density, aging properties, thermal and mechanical properties of the vulcanizates. For example in a study tilted “Curing characteristics, mechanical and thermal properties of reclaimed ground tire rubber cured with various vulcanizing systems” Krzysztof et al. [32] found that The best processing and mechanical properties for vulcanized reclaimed rubber is achievable when conventional vulcanizing system has been used to cure the vulcanizates.

The worse fatigue resistance correlates to lower amounts of polysulfidic crosslinks in the network. The CV system provide higher amounts of poly- and disulfidic crosslinks and higher proportions of sulfidic and non-sulfidic modifications. This combination provides high flex fatigue resistance but at the expense of heat and reversion resistance. Properties of CV, SEV and EV systems are shown in Table 2.4.

Table 2.1. Properties of CV, SEV and EV systems

Features	System		
	CV	SEV	EV
Poly & disulfidic crosslinks (%)	95	50	20
Mono sulfidic crosslinks (%)	5	50	80
Cyclic sulfide (conc.)	High	Medium	Low
Non sulfidic (conc.)	High	Medium	Low
Reversion resistance	Low	Medium	High
Heat aging resistance	Low	Medium	High
Fatigue resistance	High	Medium	Low
Heat buildup	High	Medium	Low
Tear resistance	High	Medium	Low
Compression set (%)	High	Medium	Low

It is evident that in many cases the use of efficient vulcanisation systems can be preferred. Improved ageing characteristics are very important since it is the factor defining the lifetime of the product. However, inferior fatigue resistance and cost considerations must be taken into consideration when it comes to choose the vulcanization system. Beside these factors in the scope of this thesis, it is planned to investigate the advantages and disadvantages of each system to assist this division making process.

2.1.7.1. Activators

Zinc oxide and stearic acid, together with sulfur and accelerator, constitute the ‘cure system’ of sulfur cure formulations. Zinc stearate is formed as result of chemical reaction between zinc oxide and stearic acid. In some cases, zinc stearate is applied directly instead of zinc oxide and stearic acid. Activators act together with accelerator to speed up the cure rate of the rubber compounds. Cure time of a compound with only elemental sulfur is at least several hours where this time reduced to minutes curing system.

2.1.7.1.1. Zinc Oxide

Since zinc oxide is used to activate the accelerator for sulfur cure, its quality and characteristics are very important. Certainly not all "zinc oxides" are the same in regards to their performance in rubber. ASTM D4295 [36] classifies zinc oxide into different performance grades based on differences in chemical characteristics [13].

1. American Process or Direct Type

This type of ZnO is produced from the reduction and reoxidation of a zinc bearing material, i.e., zinc with carbonaceous fuel. This type can have broadly varying chemical physical characteristics. Many times the nodular-type particle shape I preferred for rubber compounding. Because the properties for this type can vary greatly, it is difficult to generalize regarding its properties and characteristics.

French Process or Indirect Type

This type of ZnO is produced from the burning of zinc vapor, which is formed from the boiling of zinc metal in a retort. Since this zinc oxide is from the metal and not directly from the ore, it is characteristically more pure (better than 99.9 % pure). Usually the zinc oxide particle shape from this process is nodular in shape.

2. Secondary Zinc Oxide Type-Chemical Type

This type of zinc oxide is produced as a by-product from a chemical reaction. The properties of these types of zinc oxide can vary greatly. Its quality is greatly dependent on the source of raw material and the nature of the reaction.

Secondary Zinc Oxide Type-Metallurgical

This type is produced by burning zinc vapor from boiling scrap zinc. Since scrap zinc can vary greatly, the chemical and physical quality of this grade can also vary greatly.

In zinc oxide treatment, it is important to note that zinc oxide will commonly be treated with a fatty acid, which is usually propionic acid. This fatty acid treatment is typically about 0.5 %, which results in 0.5 % less zinc oxide. Sometimes, these treatments have been reported to improve the dispersion of the zinc oxide in certain rubber compounds.

2.1.7.1.2. Stearic Acid

Stearic acid reacts with the zinc oxide in the rubber compound to produce a salt that reacts with the rubber accelerator to initiate an effective vulcanization. Rubber grade stearic acid is not pure stearic acid. The grade of stearic acid selected as a rubber compounding ingredient is usually a mixture of stearic acid, palmitic acid, and oleic acid. The ratio of these different fatty acid components determines how they will be classified as a rubber grade "stearic acid."

Classification of rubber grades of "stearic acid" in accordance with ASTM D4817 [37] is based mainly on unsaturation level (the iodine value) and the stearic/palmitic acid ratios. A high iodine value indicates high unsaturation.

Overall, high unsaturation in a rubber grade stearic acid can affect the curing characteristics of the rubber compound. In some cases, high unsaturation can lead to higher hysteresis (heat buildup) of the vulcanizate. In addition, high levels of unsaturation can affect the solubility of the "stearic acid" in rubber leading to migration to the surface bloom or exudation.

2.1.7.2. Sulfur

Sulfur is the main component of all sulfur cure systems. Despite the poor aging performance caused by sulfur, sulfur based cure systems remained the most popular cure systems. Sulfur generally is classified into four grades for the rhombic or ordinary ground type which are general purpose, fine, oiled and conditioned and four grades for the insoluble or polymeric sulfur which are flowers of sulfur, 60 % insoluble, 90 % regular insoluble and90 % insolubles oil-treated.

The sulfur used by the rubber industry can vary in its particle size, level of oil treatment, and allotropic form (crystalline or noncrystalline). Particle size or fineness of the grind has a lot to do with how well the sulfur disperses during mixing and how uniformly it cures the rubber. Oil treatment may help reduce the risk of a sulfur fire or explosion during mixing and aid in the incorporation during the mixing process. Lastly, whether the sulfur is in crystalline (rhombic) form or the insoluble polymeric form has a great effect on the reduction or elimination of sulfur surface bloom. This is because the insoluble or amorphous sulfur grades resist being solubilized by the rubber during processing.

Therefore, at cooler temperatures after processing, there is less sulfur to separate out to the surface of the rubber forming an exudate called "bloom." This sulfur "bloom" can cause appearance problems as well as interfere with building tack and adhesion. In addition, the selection of amorphous versus crystalline sulfur can affect a compound's scorch characteristics differently.

2.1.7.3. Accelerators

The accelerator term in rubber industry, usually used to refer to an organic chemical which speeds up the rate of vulcanization. Accelerators have been introduced in 1906 and 65 years after the development of sulfur vulcanization by Goodyear. Oenslayer has discovered the effect of aniline on sulfur vulcanization however is too toxic for use in rubber products. The less toxic reaction product of aniline with carbon disulfide, thiocarbanilide, was introduced as an accelerator in 1907. Guanidine accelerators have been the next accelerators to be introduced. In 1919 dithiocarbamates, which are reaction, products of carbon disulfide and aliphatic amines find their way into the rubber market. These accelerators are still the most active accelerators in respect to both crosslinking rates and extent of crosslink formation. However, due to their low scorch resistance most dithiocarbamate accelerators cannot be used in all applications.

2-mercaptobenzothiazole (MBT) and 2-mercaptobenzothiazole disulfide (MBTS) were the first delayed action accelerators introduced in 1925.

By the introduction of first commercial benzothiazolesulfenamide in 1937 and pre-vulcanisation inhibitor (PVI) in 1968, a huge progress has been made toward faster and better-controlled vulcanization.

Some accelerators, which are also known as sulfur donner accelerators, provide sulfur from their own chemical structure. In the case of their usage need for elemental sulfur might be reduced or even eliminated. Tetramethylthiuram disulfide (TMTD), and dithiodimorpholine (DTDM) are commonly used accelerators which can simultaneously act as sulfur donner in compound formulations.

The type of elastomer chosen can dictate both the type and amount of accelerator used. For example, EPDM, with few double bonds (double bonds are used for cross-linking) needs faster curing accelerators to permit a reasonable state of cure. SBR needs a higher level of accelerators than NR.

Accelerators have been classified into six major groups according to their chemical structure as describe by ASTM D4818 [38].

2.1.7.3.1. Sulfenamides

This group of accelerators, are the principle sulfur vulcanization accelerators used in the rubber industry today. These materials has a dual role in vulcanization.

They provide scorch time (delay period) in the crosslinking or vulcanization operation at processing temperatures. The delay avoids premature crosslinking during the processing, for example, mixing, extruding, etc. at the curing temperatures these accelerators facilitate crosslinking.

These class of accelerators are sensitive to impurities and have limited storage times. No need to mention that the degradation as a result of extended storage could affect both the characteristics and performance of the accelerator.

In particular, the quality of the material is a function of storage time, temperature, relative humidity, and the impurity profile of the material; for example, free amines, salts of 2-mercaptobenzothiazole, etc. Different types of this group of accelerators have been shown in Figure 2.10.

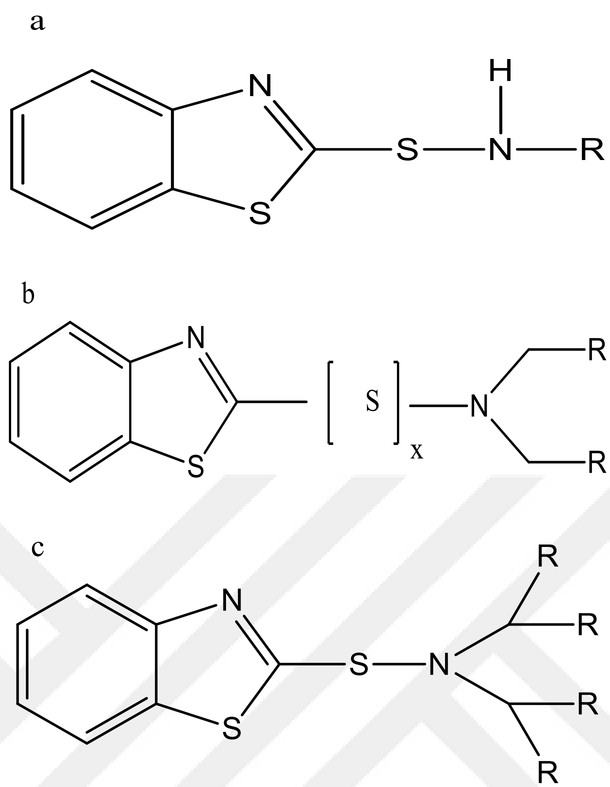

Fig. 2.4. Sulfenamides of primary amines (a), sulfenamides of unhindered secondary amines (b) and sulfenamides of hindered secondary amines

2.1.7.3.2. Thiazoles

Thiazole derivatives are versatile vulcanization accelerators that are widely used in the rubber industry either alone or in combination with other accelerators especially guanidines. Three different types of thiazoles are used commonly and they all have similar vulcanization effect. These three thiazoles are Mercaptobenzothiazole (MBT), Zinc Salt of 2-Mercaptobenzothiazole (ZMBT) and Dibenzothiazyldisulfide (MBTS) and are presented in Figure 2.11.

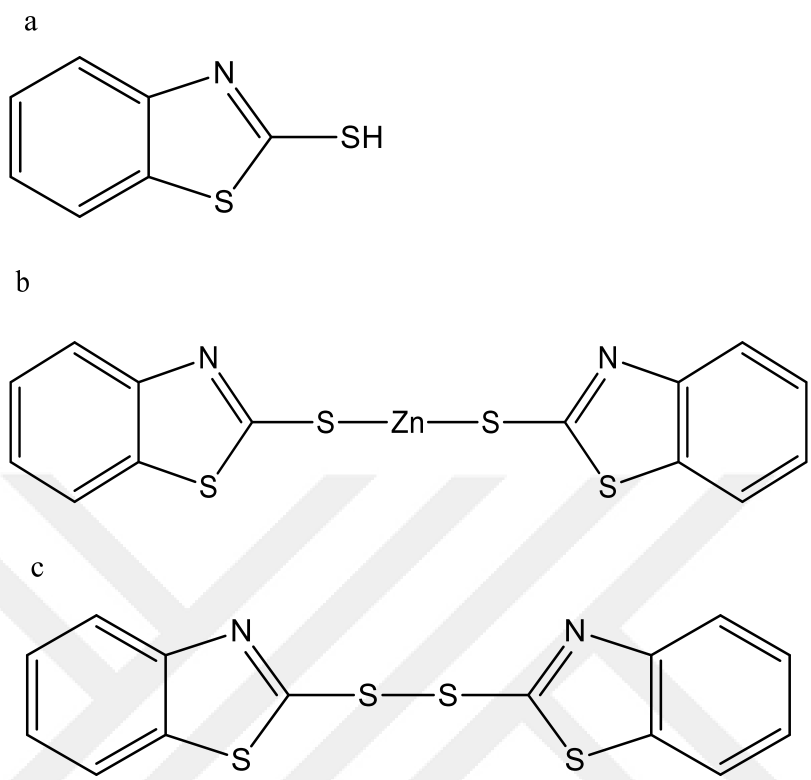

Fig. 2.5. Mercaptobenzothiazole (a); Zinc Salt of 2-Mercaptobenzothiazole (b) and Dibenzothiazyldisulfide(c).

2.1.7.3.3. Guanidines

The guanidines are not normally used as primary accelerators, except for thick-sectioned goods. This is related to their slow rate of acceleration. Together with other accelerator groups, especially thiazoles they are used as secondary accelerator. This will result to faster and higher levels of vulcanization compared to their individual usage. The thiazole-guanidine combinations are frequently used for technical rubber goods.

There are two different types of guanidines in common use with a similar vulcanization efficiency. These two types are symmetric (Type I) and asymmetric (Type II).

Diphenylguanidine (DPG) and di-ortho-tolyguanidine (DOTG) are examples of Type I, while Orthotolybiguanidine (OTBG) is an example of type II that are presented in Figure 2.12.

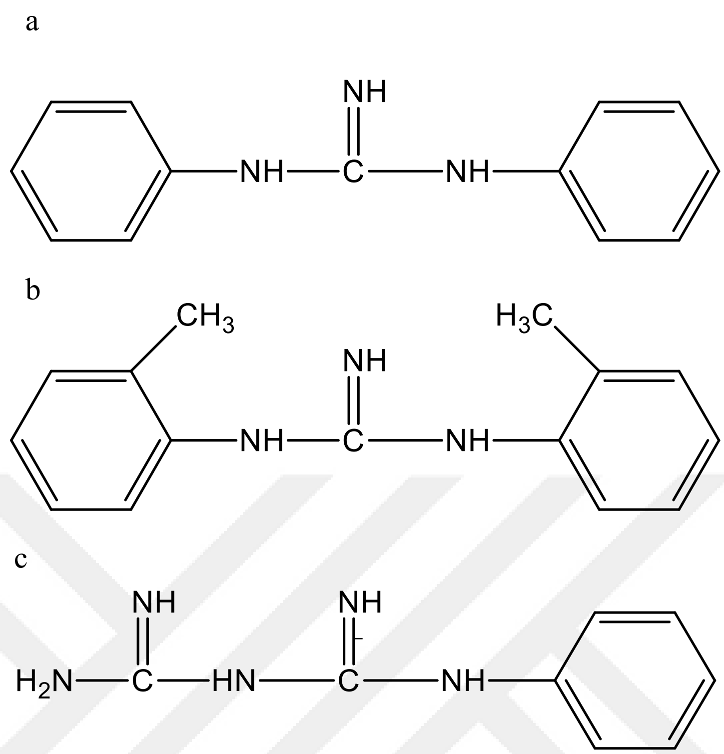

Fig. 2.6. Diphenylguanidine (a), di-Ortho-tolyguanidine (b) and orthotolybiguanidine (c)

2.1.7.3.4. Dithiocarbamates

Vulcanization with dithiocarbamates is faster than with thiurams. Dithiocarbamates are used as ultra-accelerators with normal sulfur levels. They are also employed as secondary accelerators or activators for other accelerators. Figure 2.13 shows the general structure of dithiocarbamate accelerator types. Where R' represents alkyl groups such as amyl, butyl, ethyl, or methyl, or aryl groups such as phenyl or benzyl; R'' represents alkyl groups such as amyl, butyl, ethyl or methyl, or aryl groups such as phenyl or benzyl; M represents metals such as zinc, tellurium, copper, cadmium, nickel, bismuth, or lead. n = 2 in the case of zinc, copper, cadmium, nickel, and lead. n = 3 in the case of bismuth and n = 4 in the case of tellurium or selenium.

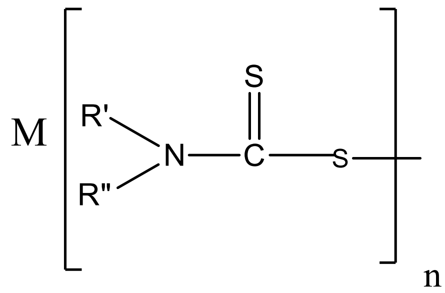

Fig. 2.7. General structure of dithiocarbamate type accelerators.

2.1.7.3.5. Thiurams (disulfides)

Thiuram disulfide accelerators are used for vulcanization, without elemental sulfur, to produce rubber compounds, which show essentially no reversion and which have low compression set and good aging characteristics. For low sulfur vulcanization, thiurams are normally used in combination with sulfenamides. With a normal amount of sulfur, thiurams act as ultra-accelerators. Figure 2.14 shows general structure of thiouram disulfide type accelerators. When R' = R" = methyl then the accelerator will be tetramethyl thiuram disulfide (TMTD), when R' = R" = ethyl then the accelerator will be tetraethyl thiuram disulfide (TETD), and if R' = methyl R" = phenyl then the accelerator will be dimethyl diphenyl thiuram disulfide (DMPTD)

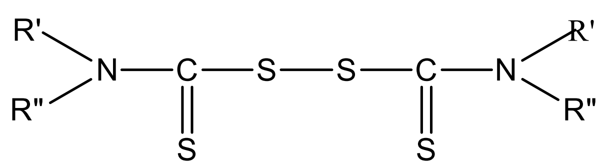

Fig. 2.8. General structure of thiouram (disulfide) type accelerators.

2.1.7.3.6. Thiurams (other than disulfides)

This class contains other thiuram types, which are not disulfides. They are used as ultra-accelerators with normal amounts of sulfur. Di, tetra, and hexasulfides can be employed without sulfur or with low sulfur levels to obtain rubber compounds with much reduced reversion tendencies. Figure 2.15 shows general structure of thiouram (other than disulfide) type accelerators. When R' = R'' = methyl then the accelerator will be tetramethyl thiuram monosulfide (TMTM).

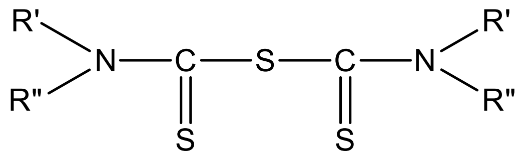

Fig. 2.9. General structure of thiouram (other than disulfide) type accelerators.

2.2. Compound Formula

A basic raw rubber compound is a curable mixture of elastomer/elastomer (raw gum rubber), fillers, activators, accelerators, antidegredants, plasticizers and sulfur, which are all selected in the way to optimize the properties according to final product application area. The phr unit, which is used in compound formulations, stands for parts per hundred part of raw, gum elastomer. Table 2.4 is a presentation of a typical compound formula.

Table 2.2. A typical compound formula

Material	phr
Raw gum elastomer	100
sulfur	0-4
Zinc oxide	5
Stearic acid	2
Accelerators	0.5-3
Antioxidants	1-3
Fillers	0-150
Plasticizers	0-150

3. EXPERIMENTAL

3.1. Chemicals

Natural rubber (NR) and Chloroprene rubber (CR) have been used as main component in all the prepared compounds. Standard Malesian Rubber (SMR 20) with Plasticity retention index (PRI) of 40 and ash content of 0.8% and CR with Mooney viscosity of 45–53 ML1+4 (100°C) and 500% modulus value of 1–4 MPa, which has been obtained from Elkim, Turkey have been used to prepare rubber compounds. The used carbon black N330 was high-abrasion furnace (HAF) type that had been obtained from Anex, Turkey. Naphthenic process oil (Octopus N418) with viscosity–gravity constant of 0.855 has been purchased from Petroyağ, Turkey. Other compounding ingredients were traditionally used commercial rubber additives and accelerators; tetramethyl thiuram disulfide (TMTD), 2-mercaptobenzothiazole (MBT), diphenyl guanidine (DPG), zinc dibutyl dithiocarbamate (ZDBC) and N,N'-diethylthiourea (DETU) purchased from RPM Prod, Turkey.

3.2. Machinery Used For Compounding & Curing

3.2.1. Banbury (Internal mixer)

An internal mixer (Banbury) with 4 L total volume manufactured by Met-Gür (Turkey) has been used in compounding procedure (shown in Figure 3.1). The machine has two tangential rotors and variable rotation speed ranging from 11-37 rpm.

Fig. 3.1. Met-Gür’s 4 L Banbury

3.2.2. Laboratory Press

Brabender's Polystate 200T model (shown in Figure 3.2) hot press has been used to cure the prepared compounds. This press provides hydraulic pressure up to 400 bar and working temperature up to 300°C.

Fig. 3.2. Laboratory hot press

3.3. Machinery Used For Testing & Analysis

3.3.1. Moving Die Rheometer (MDR)

All the rheological analysis have been carried out using Alpha Technologies MDR 2000B model a rheometer (shown in Figure 3.3) according to ASTM D5289 [39] standard. This machine is capable of measuring rubber compound cure under isothermal test conditions with constant strain (0.5°) and frequency (1.667 Hz). A constant volume sample cutter also has provided by Alpha technologies, which can cut the samples to a constant volume and weight of approximately 5 grams.

Fig. 3.3. MDR 2000-B Moving Die Rheometer

3.3.2. Universal Testing Machine

Zwick's Z010 universal testing machine (shown in Figure 3.4) has been used to perform tensile tests. The machine can operate at ambient temperature range of 10-35°C and humidity range of 20-90%. Zwick's ZC020 cutting press has been used to cut samples into dog bone shape according to ASTM D412 [40] type D. The dog bone shaped sample dimensions have been presented in Figure 3.5.The tests have also been carried out according to ASTM D412.

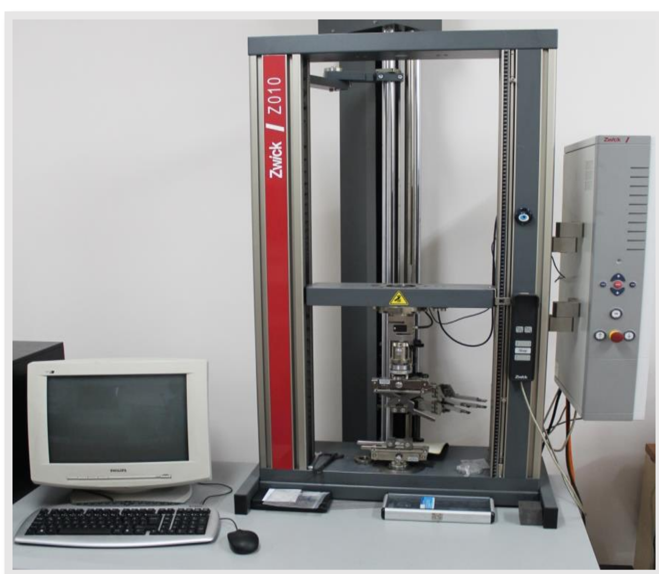

Fig. 3.4. Zwick Z010 Universal Testing Machine

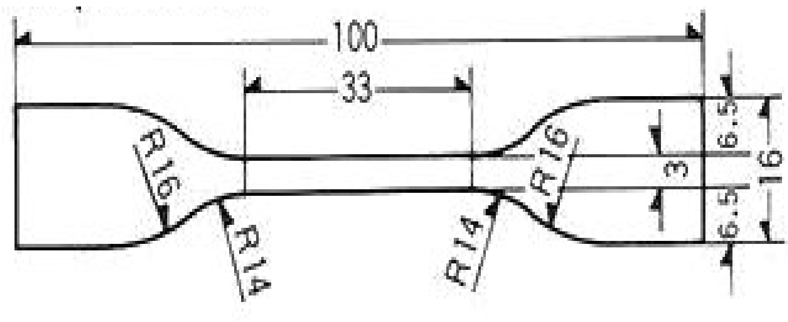

Fig. 3.5. ASTM D412 type D specifications

3.3.3. Pulse NMR Analyzer

Bruker's Minispec mq20 pulse NMR analyzer (shown in Figure 3.6) which operates at 20 MHz frequency has been used to calculate crosslink density of the samples. The magnet and probe temperature and recycle delay time have been set to 40°C and 1 s, respectively. Gain value has been optimized so that the free induction decay curve that starts between 60% and 90%. Hahn echo decay principle has been followed to determine XLD using T2 relaxation time. Data analysis has been carried out using OriginLab 9 software.

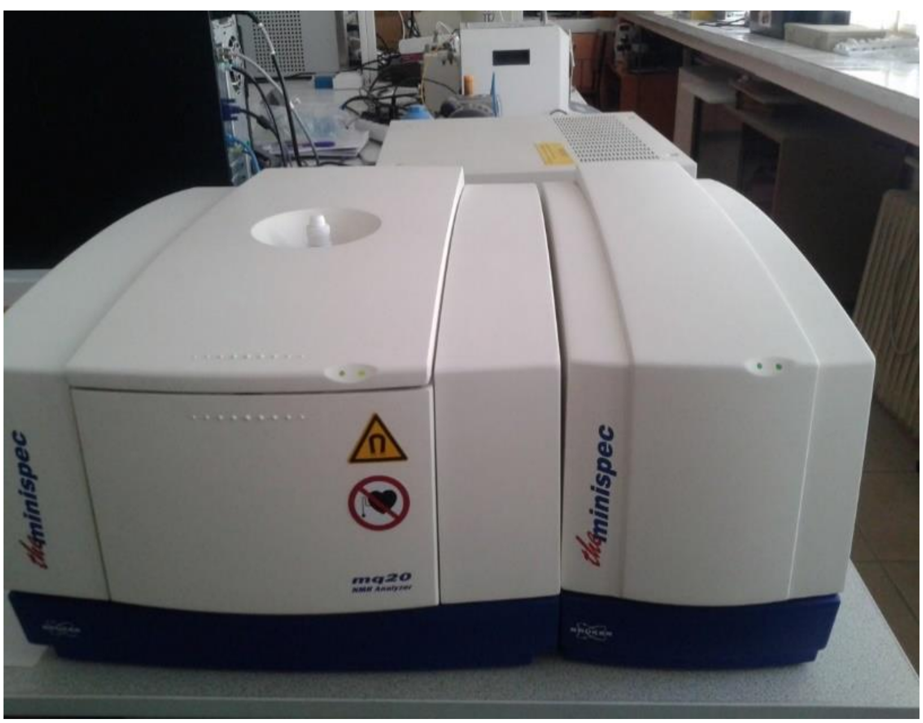

Fig. 3.6. Pulse-NMR equipment

3.3.4. Temperature Scanning Stress Relaxation (TSSR) Meter

Temperature scanning stress relaxation tests have been performed using TSSR-meter instrument obtained from Brabender (Figure 3.7). TSSR-meter has a heating/cooling chamber with electric heating and air-cooling, operation temperature range of 20 - 300°C and heating rate of 0 - 4 K/min. This machine uses the samples cut according to ASTM D412 type D to perform a two-step analysis on the samples. The relaxation curves of isothermal first step and un-isothermal second step are both available separately for further analysis.

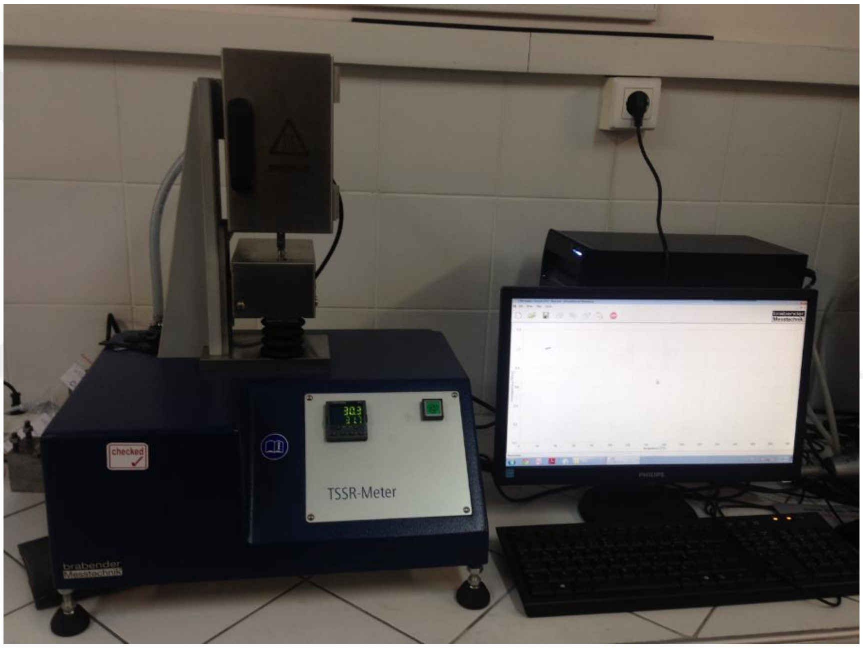

Fig. 3.7. TSSR-meter instrument

3.4. Accelerated Weathering Tester

Q-Lab's QUV accelerated weathering tester have been used to perform accelerated aging tests on the vulcanizates. The accelerated weathering tester (Figure 3.8) reproduces the damage caused by sunlight, rain and dew in a standard controlled manner. In course of few days, this machine is able to reproduce the damage that occurs over months or years outdoors.

To simulate outdoor conditions, the accelerated weathering tester exposes materials to alternating cycles of UV light and moisture at controlled, elevated temperatures. It simulates the effects of sunlight using special fluorescent UV lamps. It simulates dew and rain with condensing humidity and/or water spray. In our tests, we have used UVA-340 lamps mounted into this machine that give the best simulation of sunlight in the critical short wavelength region from 365 nm down to the solar cut-off of 295 nm. The test have been carried out according to ASTM G154 [41].

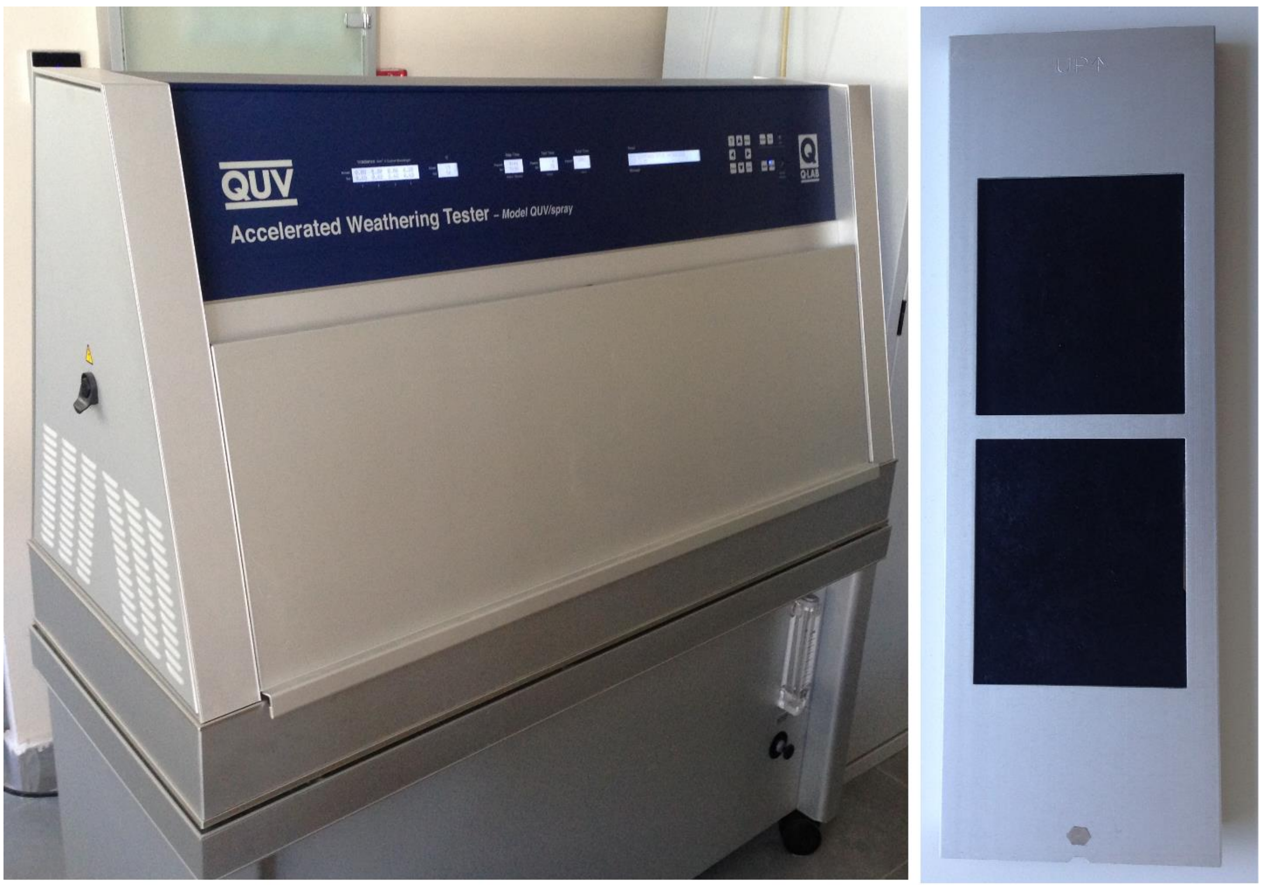

Fig. 3.8. Accelerated weathering tester machine (left) & its sample holder (right)

3.5. Compounding

3.5.1. Formulations of the Compounds

The NR/CR based compounds have been prepared according to the formulations that have been presented in Tables 3.1-3.3. The main goal here is to find out the differences caused by each of sulfur vulcanization systems and each accelerator type.

Table 3.1. Formulations of the blends as for conventional vulcanization system (CV)

	CV-TMTD	CV-MBT	CV-DPG	CV-ZDBC	CV-DETU
	Composition (phr)				
Natural Rubber	80	80	80	80	80
Chloroprene Rubber	20	20	20	20	20
Carbon Black N330	65	65	65	65	65
Naphthenic Oil	10	10	10	10	10
ZnO	5	5	5	5	5
MgO	2	2	2	2	2
Stearic Acid	2	2	2	2	2
TMQ	1.5	1.5	1.5	1.5	1.5
IPPD	0.5	0.5	0.5	0.5	0.5
Paraffinic Wax	2	2	2	2	2
TMTD	0.5				
MBT		0.5			
DPG			0.5		
ZDBC				0.5	
DETU					0.5
Sulfur	3.5	3.5	3.5	3.5	3.5

Table 3.2. Formulations of the blends as for semi-efficient vulcanization system (SEV)

	SEV-TMTD	SEV-MBT	SEV-DPG	SEV-ZDBC	SEV-DETU
	Composition (phr)				
Natural Rubber	80	80	80	80	80
Chloroprene Rubber	20	20	20	20	20
Carbon Black N330	65	65	65	65	65
Naphthenic Oil	10	10	10	10	10
ZnO	5	5	5	5	5
MgO	2	2	2	2	2
Stearic Acid	2	2	2	2	2
TMQ	1.5	1.5	1.5	1.5	1.5
IPPD	0.5	0.5	0.5	0.5	0.5
Paraffinic Wax	2	2	2	2	2
TMTD	2				
MBT		2			
DPG			2		
ZDBC				2	
DETU					2
Sulfur	2	2	2	2	2

Table 3.3. Formulations of the blends as for semi-efficient vulcanization system (EV)

	EV-TMTD	EV-MBT	EV-DPG	EV-ZDBC	EV-DETU
	Composition (phr)				
Natural Rubber	80	80	80	80	80
Chloroprene Rubber	20	20	20	20	20
Carbon Black N330	65	65	65	65	65
Naphthenic Oil	10	10	10	10	10
ZnO	5	5	5	5	5
MgO	2	2	2	2	2
Stearic Acid	2	2	2	2	2
TMQ	1.5	1.5	1.5	1.5	1.5
IPPD	0.5	0.5	0.5	0.5	0.5
Paraffinic Wax	2	2	2	2	2
TMTD	3.5				
MBT		3.5			
DPG			3.5		
ZDBC				3.5	
DETU					3.5
Sulfur	0.5	0.5	0.5	0.5	0.5

There for in each of these formulations all the other components have been kept constant varying only accelerator type and then accelerator to sulfur ratio (vulcanization system). The accelerator to sulfur ratio is 0.5:3.5 for conventional system 1:1 in semi efficient system and 3.5:0.5 in efficient system. Accelerators have been chosen to reflect the properties of the groups that are represent as described in section 2.1.7.3.

3.5.2. Mixing Procedures

Natural rubber pieces have been masticated for 4 minutes and the mixed with chloroprene pieces for 2 minutes more. Carbon black and process oil have been added to the mixture with 1 min intervals and in 3 lots to aid the mixing process. After mixing for 5 minutes more, activators and stabilizers have been added and mixed for additional 4 minutes. The mixture has been dropped and cooled down in ambient conditions to reach the temperature of 40°C and the loaded into the bunbury mixer, again. The cure additives have been added and mixed for 5 minutes before the last drop. Through all the mixing procedure, the temperature has been monitored carefully not to be above 60°C to prevent scorch. The raw rubber compounds have been shaped into 2 mm sheets and stored in room temperature for 48 hours before being tested for rheological parameters. Then to prevent any unwanted curing or thermal aging effect the remaining uncured compounds have been stored in refrigerator took out hours before curing and other tests.

3.6. Analysis Methods

3.6.1. Analyzing Cure State Using Moving Die Rheometer

The oscillating die rheometer (ODR) and the moving die rheometer (MDR) have been developed and marketed by Monsanto, the MDR being introduced in 1985.

In the MDR, a thin sheet of rubber, about 2 mm thick, is placed between the two dies kept at the desired temperature; the lower disc oscillates and a reaction torque/pressure transducer is positioned above the upper disc. It has been found that the MDR gives shorter times of cure than the ODR because of better heat transfer and higher torque values, owing to the die design.

Another reason may come from a different thickness of the rubber sample. A typical torque–time curve obtained with these two apparatus, which is shown in Figure 3.9, clearly indicates this strong difference. Both of these machines work under isothermal conditions.

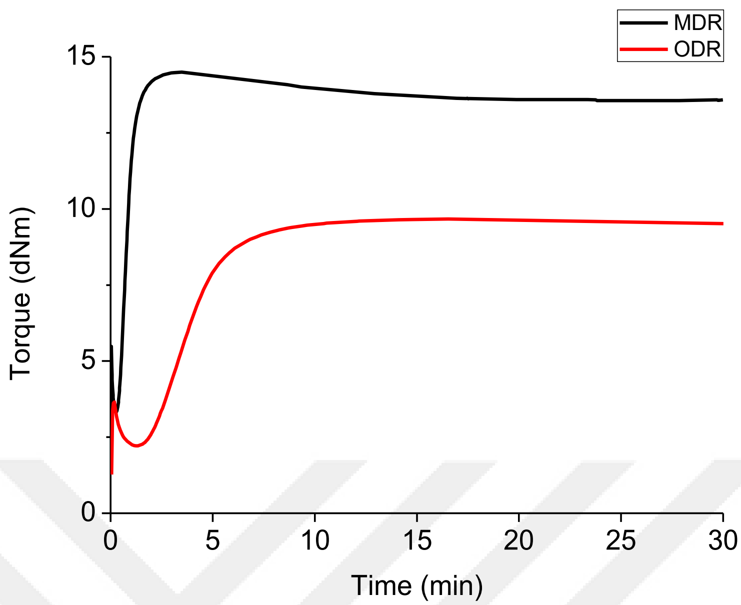

Fig. 3.9. Typical torque–time curves obtained with the oscillating disc rheometer (ODR) and with the moving die rheometer (MDR) with the same rubber compound

There are some important test characteristics, which are used to evaluate state of cure using MDR testing machine;

ML minimum torque--Relates crudely to processability of the rubber compound.

MH maximum torque--Relates to the ultimate crosslink density that results from the vulcanization process.

t_s2 scorch time--Time till 2 Mooney units rise above the minimum that is a measure of scorch safety time.

t 90 optimum cure time--This is the time required for the compound to reach 90 % of the total state of cure. This is a value for obtaining cure rate and optimum cure time at a specified temperature

Cure extent or Δ torque (MH-ML) is commonly used in rubber industry and believed to relate more in pure chemical crosslinking, where ML relates to the uncured physical crosslinking (or chain entanglements).

Cure Rate Index (CRI), calculated from the scorch point and t_{90} as shown in Equation 3.1.

$$CRI = 100/(t_{90} - ts2) \quad (3.1)$$

If the compound is faster curing, then the difference between t_{90} and ts2 will be less and the calculated CRI will be higher. If the compound is slower curing (has a slower average cure rate), the opposite will be true.

Analyzing the MDR curves one should pay special attention to the general shape of the curves. From this point of view, curves have been placed in three different types.

Cure curves that plateau, those that revert, and those that march.

Rubber compounds in Plateau forming category reach the ultimate state of cure (ultimate crosslink density) without any additional chemical crosslinking reactions occurring.

Natural rubber formulations are one example of compounds that will revert if the cure temperature is high enough (2^{nd} Category). Many times, a competing reaction is also occurring during the vulcanization reaction. Usually if the cure test is performed at a lower temperature, there will be less reversion but the test will take longer duration. 3^{rd} category curve has ever increasing modulus and never forms a plateau. Some EPDM compounds will give this type of cure profile. At some point in the cure test, you have to decide to stop because it will never truly plateau.

Therefore, in order to make a good analysis according to the obtained data from MDR, one should combine the data obtained from the software and general shape of the curve.

3.6.2. Analyzing Crosslinking Density Using Pule NMR Technique

Nuclear magnetic resonance spectroscopy is a well stablished technique in modern chemistry. In 1947 and shortly after the discovery of nuclear resonance in bulk matter, it was discovered that natural rubber gives a proton line width more like that of a liquid than of a solid at room temperature. Because of the narrower resonance line width in liquid state, this technique is completely different from solid state NMR from spectral resolution aspect. Anisotropic spin interactions, which take place in solids, is the well-known reason for this phenomenon. The molecular motion in an isotropic liquid effectively removes many of the nuclear spin interactions, which leads to simple NMR spectra.

From the early 70's Pulse NMR technique which also known as longitudinal relaxation, has been modified and used by Charlesby et al. to investigate crosslinking and entanglements in macromolecules [42, 43]. They have successfully used this technique to investigate crosslinking in irradiated polyisobutylene and other plastics. Later Pulse NMR technique has been applied to determine crosslink density of elastomers [44]. Kuhn et al. has applied pulse NMR to determine crosslink density of elastomers [45, 46]. In these works, they have tried to clarify effect of sulfur, accelerator and activator amounts on crosslink density of the elastomers and also prove the efficiency of the method for the elastomers. Actually, this method is one of the fastest and most reliable methods to calculate XLD of the elastomers and investigate the aging effects [47]. Vieyres et al, in their study which is titled "Sulfur-Cured Natural Rubber Elastomer Networks: Correlating Cross-Link Density, Chain Orientation, and Mechanical Response by Combined Techniques", have compared and combined pulsed NMR, equilibrium swelling and mechanical test results to get network structure details for unfiled elastomers. In pulse NMR method spin-lattice relaxation (T1) and spin-spin relaxation (T2) times have different values. The study of T1 and T2 can lead to valuable knowledge about molecular structure and molecular motion. T2 relaxation time is related to the polymeric structure and dynamics. The ratio of proton spins, which can align parallel or anti-parallel to the external magnetic field, is given by the Boltzmann distribution and is near 1. Transversal magnetization can be created by applying an additional magnetic field B1 that is perpendicular to B0. This B1 field is actually a radio frequency pulse. If the radiation frequency is equal to the Larmor frequency of the nuclei the field causes a rotation of the equilibrium magnetization around the x axis. Immediately the magnitude of the bulk magnetization starts to decrease because of the effect of dephasing due to inhomogeneity of B0. The spins experiencing a stronger local magnetic field than B0 will process faster than the bulk magnetization.

Experimentally we record the free induction decay (FID) G(t) which is actually the quantity of transverse magnetization as a function of time and it can be defined as;

$$G(t)=M(t)/M(0) \qquad (3.2)$$

Above the glass transition temperature, the system of protons may be approximately considered as a collection of isolated spin pairs attached to polymer chains' backbones. Fast uncorrelated motion generates a slow-decaying signal.

The entire network executes a slow, probably isotropic movement. The intercrosslinked chains are fixed at both ends by chemical crosslinks and show fast anisotropic movements. Small molecules (such as free dangling ends, wax and solvents) on the other hand, show liquid like isotropic fast molecular movements that are characterized by exponential signal decay.

To calculate crosslinking density of rubbers according to this technique, first the FID curves must be obtained applying he pulse program and then the curves must be fitted to Equation 3.3 due to Hahn-Echo-Decay principle.

$$M(t) = A \exp(-t / T_2 - (q M_2 t^2) / 2) + B \exp(-t/T_2) \quad (3.3)$$

where M(t) is the detected signal, corresponding to the magnetization, A and B are respective amplitudes of the crosslinked and highly mobile fractions of the polymer in total signal [48], T_2 is spin-spin relaxation time and M_2 is the dipolar moment, a quantity reflecting the strength of the dipolar coupling below the glass transition temperature.

q is the motion factor and its values can vary between 0 and 1 where 0 value of q represents fully isotropic fast molecular motions and 1 represents totally rigid polymer chain motions.

After obtaining the q_0 (from fitting the FID curve data of uncured compound) and q values, Equation 3.4 can be used to calculate crosslinking density of the vulcanizates.

$$M_c = \frac{3}{5\sqrt{q-q_0}} C_\infty \frac{M_{RU}}{N} \quad (3.4)$$

M_c is averaged inter-crosslink chain mass, q_0 is q-value of uncured sample, c is backbone units per Kuhn-segment, M_{RU} is average molar mass of one monomeric units and N is backbone bonds per monomeric unit. Then the crosslinking density can be calculated by dividing the density of samples to M_c values.

All of the vulcanizates have been cut into small pieces (3-5 mm diameter, 2 mm thickness and 6-8 mm length). The magnet and probe temperature and recycle delay time have been set to 40°C and 1 s respectively. The gain value has been optimized so that the free induction decay (FID) curve starts between 60-90%. Hahn-Echo-Decay principle has been followed to determine crosslink density (XLD) using T2 relaxation time.

3.6.3. Analyzing Stress Relaxation Behavior Using Temperature Scanning Stress Relaxation Technique

Stress relaxation behavior of rubbers have been studied since 40s. Tobolsky et al. have studied stress relaxation of natural and synthetic rubbers[49]. They found out that the degradation activation energy especially in the case of natural rubber is independent of the elongation, and of the presence of carbon black. They also found that the effect of temperature on the relaxation of stress appeared to be of the general type characteristic of chemical reactions. In 1965 Cotton and Boonstra have tried to establish an empirical equation relating decrease in tension to relaxation time [50].

Polymers exhibit a time dependent decrease of stress when they are exposed to a constant strain. This phenomenon is known as stress relaxation. The microscopic mechanisms, leading to the macroscopic recognizable decrease of stress, may result from physical and/or chemical processes.

The relaxation time constant τ as described by Maxwell model is the time passed until the stress has dropped down to the value of σ_0/e. σ_0 indicates the initial stress at time zero when the strain has been applied to the sample. However, this model fails to describe complicated behavior of elastomers.

The theory of linear viscoelasticity, uses generalized Maxwell model to describe relaxation process. This theory uses an infinite number of individual spring-dashpot elements. The relaxation modulus E_{iso} is a function of time when relaxation takes place under isothermal conditions as formulated in Equation 3.5 [51].

$$E_{iso}(t) = E_\infty + \int_{-\infty}^{\infty} H'(\tau).e^{\frac{-t}{\tau}}\,dln\,\tau \tag{3.5}$$

The relaxation modulus can be calculated by dividing the observable stress σ(t) by the applied strain ε_0. The relaxation spectrum $H'(\tau)$ is a steady function describing the probability of the relaxation time constants τ of the model.

The constant E_∞ is added to equation 3.5 to allow the system to approach an equilibrium state higher than zero, as observed normally for viscoelastic solids.

According to Alfrey's rule the value of the relaxation spectrum at point τ = t is obtained in first approximation by differentiating E_{iso}(t) with respect to ln t, by Equation 3.6.

$$H'(\tau) = -\left(\frac{\mathrm{d}E_{iso}}{\mathrm{dln\,t}}\right)_{\mathrm{t=\tau}} = -t\,.\left(\frac{\mathrm{d}E_{iso}}{\mathrm{dt}}\right)_{\mathrm{t=\tau}} \tag{3.6}$$

It is practically impossible to determine the entire function by means of a single stress relaxation measurement since the relaxation spectrum is time dependent. To create a master curve, based on time temperature superposition (TTS) principle, a set of measurements at different temperatures must be carried on. This is exactly where the idea of single experiment with constant rate of temperature increase comes to help.

Vennemann et al., have recently introduced an alternative strategy called temperature scanning stress relaxation (TSSR), in order to find a way to determine the entire function with a single relaxation measurement.

In contrast to traditional isothermal tests, during TSSR measurements the temperature is not kept constant, but is increasing linearly with a constant heating rate β. As a result, the non-isothermal relaxation modulus $E_{non\text{-}iso}$ is obtained as a function of temperature. Analogue to isothermal stress relaxation measurements, the spectrum H(τ) can be calculated in first approximation by Equation 3.7 [52].

$$\mathrm{H(t)} = -\Delta T\left(\frac{\mathrm{d}E_{non-iso}}{\mathrm{dT}}\right)_{\beta=\frac{\Delta T}{t}=const} \tag{3.7}$$

In this equation, T_0 stands for the initial temperature at which the test is started; and β is the heating rate of the temperature scan. Although this function is not defined on time scale, the relaxation mechanisms of the polymer sample undergoes during the test can be identified clearly, because the relaxation time constant τ decreases monotonously with increasing temperature T. Due to its very strong temperature dependence, the relaxation time constant drops down to small values rapidly, within small temperature range. Thus, the entire spectrum is observable on temperature scale within a relative short period during a temperature scan of a TSSR test.

While stress relaxation is being analyzed, thermal expansion and rubber have to be taken into consideration. The initial sample length l_0 will increase due to the temperature raise from start temperature T_0 to the temperature T. In consequence, the thermal expansion of the sample contributes to a decrease of stress, if a stretched sample is mounted between sample holders with a constant distance. The thermally induced variation of strain $\varepsilon = (l - l_0)/l_0$ during TSSR tests can be easily calculated by Equation 3.8.

$$\epsilon\,(T) = \frac{l}{l_0(1+\alpha\Delta T)} - 1 \quad (3.8)$$

Where L_0 is the initial distance of the sample holders at temperature T_0 and α is the coefficient of linear thermal expansion of the sample. For rubber typical values for α are in the range of 1 to 3. 10^{-4} K^{-1} [53].

The influence of temperature on relative strain becomes negligible, when the strain is sufficiently high. To minimize the influence of thermal expansion, TSSR experiments should be performed at initial strains not below 50 %.

The mechanical stress σ is proportional to the absolute temperature T in case of an ideal rubber network, expressed by Equation 3.9

$$\sigma = \nu\,\mathrm{RT}\,(\lambda - \lambda^{-2}) \quad (3.9)$$

Here v is crosslink density of the network and R is the universal gas constant. The strain ratio λ is defined as $\lambda = l/l_0$, where l is the length and l_0 the initial length of the sample.

According to equation 3.9, the stress should increase with increasing temperature, if the strain ratio λ is kept constant. The slope of the stress-temperature curve at constant elongation can be obtained from the derivative of stress with respect to temperature, which is assigned as temperature coefficient κ in the following.

$$\kappa = \left(\frac{\partial\sigma}{\partial \mathrm{T}}\right)_{\lambda} = \nu\,\mathrm{R}\,(\lambda-\lambda^{-2}) \quad (3.10)$$

Considering the temperature dependence of the strain, as described by equation 3.8, the relation of 3.9 can be rewritten as

$$\sigma = \nu\,\mathrm{RT}\left(\frac{\lambda_0}{1+\alpha\Delta\mathrm{T}} - \left(\frac{\lambda_0}{1+\alpha\Delta\mathrm{T}}\right)^{-2}\right) \quad (3.11)$$

where λ_0 is the initial strain ratio at temperature T_0. Compared to the uncorrected curve resulting from equation 3.9, initial slope is slightly reduced due to thermal expansion and the function is no longer strictly linear, but exhibits a slight curvature with increasing temperature. So the corrected value of κ, which is a function of temperature, can be calculated by derivation of equation 3.11 with respect to temperature T as it is given by equation 3.12

$$\kappa_0 = \kappa(T_0) = v\,R\,((\lambda_0 - \lambda_0^{-2}) - T_0 \propto (\lambda_0 + 2\lambda_0^{-2})) \qquad (3.12)$$

With this regard, crosslink density can be calculated form TSSR experiments, theoretically. But as we will see from the test result, this is not the case at least for NR/CR vulcanizates where the true value of κ and therefore XLD could not be calculated for almost any of the samples.

The TSSR instrument consists of an electrical heating chamber where the sample, a S2 testing rod, is placed between two clamps. The clamps are connected to a linear drive unit to apply a certain uniaxial extension to the sample. A high quality signal amplifier in combination with a high resolution AD-converter is used to detect and digitize the analogue signals of the high-resolution force transducer and the thermocouple [51].

The test method is a three-step procedure. First step is application of initial stress at 23°C. To minimize the influence of thermal expansion, TSSR experiments should be performed at initial strains (ε_0) not below 50 %. The second step which is isothermal relaxation starts write after the first step and continues for two hours. Then the heating step starts at the rate of β = 2 K/min until the complete relaxation or rupture of the sample.

From the obtained force-temperature curve certain characteristic quantities such as T_X (the temperature at which the force ratio F/F_0 has decreased about x% with respect to the initial force F_0) and the TSSR index (RI) can be calculated. The TSSR index (RI) is a measure of the rubber like behavior of the material and is calculated from the area below the normalized force-temperature curve.

This method has been used successfully to investigate relaxation behavior, network structure and service temperatures of thermoplastic elastomers [54-56] .

4. RESULTS & DISCUSSION

As it has mentioned in Section 2, natural rubber has advantages like excellent dynamic performance and unique stress relaxation and abrasion qualities, which makes it the most popular industrial rubber type. However, as it is known its poor weathering and ozone resistance is always a challenge for scientist and engineers, who are trying to reach the maximum durability, in severer conditions. Chloroprene rubber on the other hand has good chemical stability and can maintain its flexibility over a wide temperature range. Therefore a good formulated compound containing these two rubbers theoretically can combine advantages of these rubbers together. Literature provides proof for this assumption. For example Dikiciler et al. have been used different amounts of chloroprene rubber together with natural rubber and find out the optimum ratio of these rubbers [57] In the scope of this thesis, these two rubbers have been chosen to end up with vulcanizate that can exhibit good elasticity and performance in a wide temperature range. To fill the literature gap in regard of vulcanization system and accelerator effect on network structure, NR/CR compounds has been formulated to vary in accelerator type and accelerator to sulfur ratio (vulcanization system). Since rubber durability measured regarding the mechanical performance and in turn, this performance is related to the network structure of the rubber, a series of analysis have been organized to reveal this dependency. In this regard, all the compounds have been formulated, mixed, cured and tested according the procedures that have been explained in section 3. The following part of this section describes the results in detail.

4.1. Effect of Accelerator Type and Cure Systems on Cure Rate of NR/CR Vulcanizates

All the of the uncured rubber compounds, which have been prepared according to the process described in 3.3.1.1 and 3.3.1.2, have been kept at room temperature for 48 hours and then tested using MDR type rheometer according to ASTM D5289. The tests have been performed at 170°C and for 30 min. Total cure time and temperature have been optimized after several test have been performed at 160,165, 170, 175°C and 20, 30, 40, 50 min. Optimum cure time and temperature have been set according to the scorch and reversion areas of the obtained curves. As it was discussed in Section 3.3.2. Rheometer curves for the TMTD, MBT, DPG, ZDBC and DETU-accelerated compounds in different cure systems have been shown in Figures 4.1-4.5, respectively.

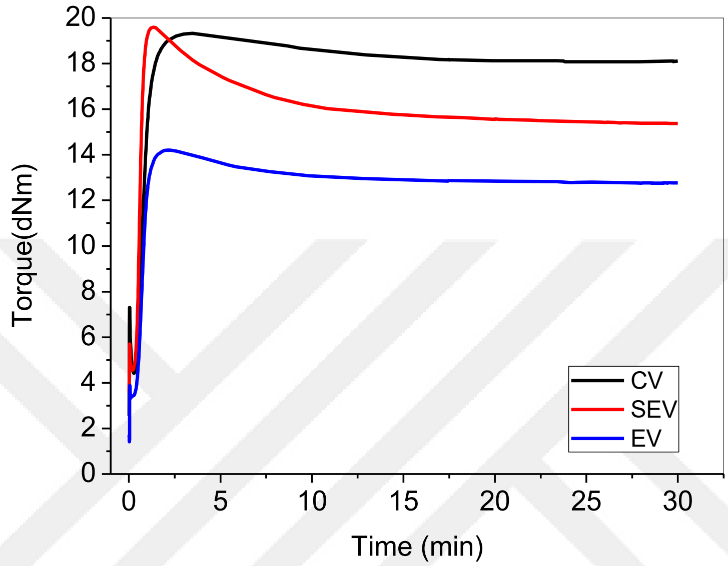

Fig. 4.1. Rheometer curves of TMTD-accelerated compounds for CV, SEV and EV systems

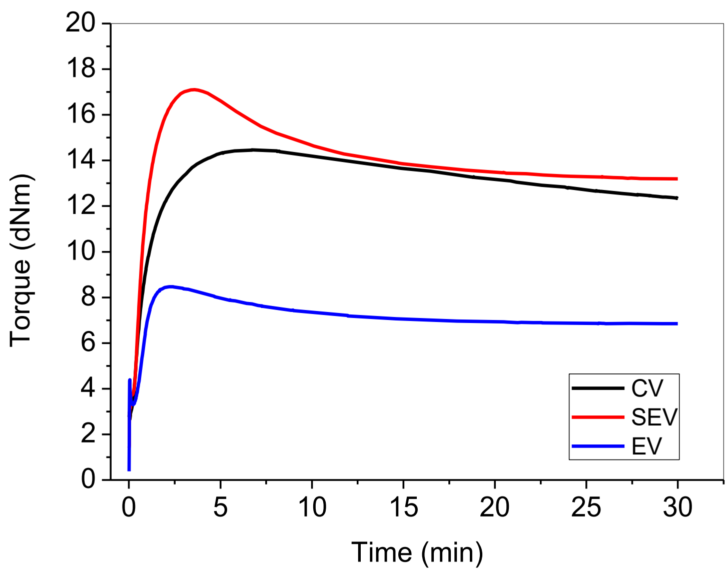

Fig. 4.2. Rheometer curves of MBT-accelerated compounds for CV, SEV and EV systems

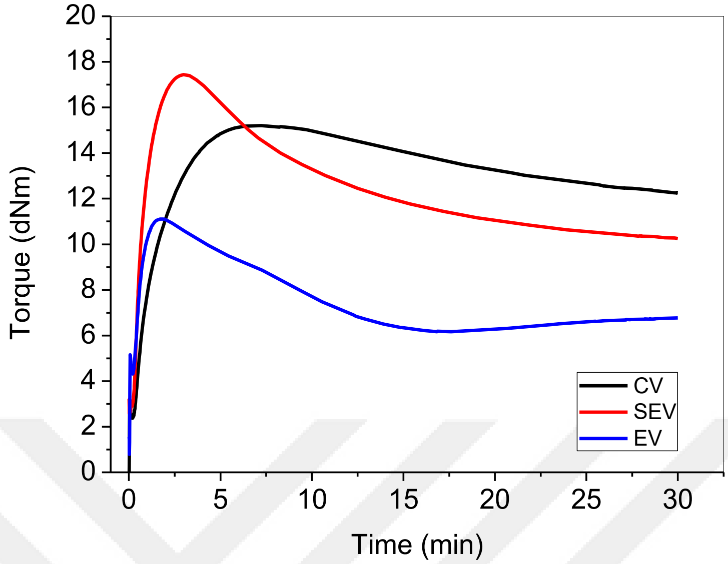

Fig. 4.3. Rheometer curves of DPG-accelerated compounds for CV, SEV and EV systems

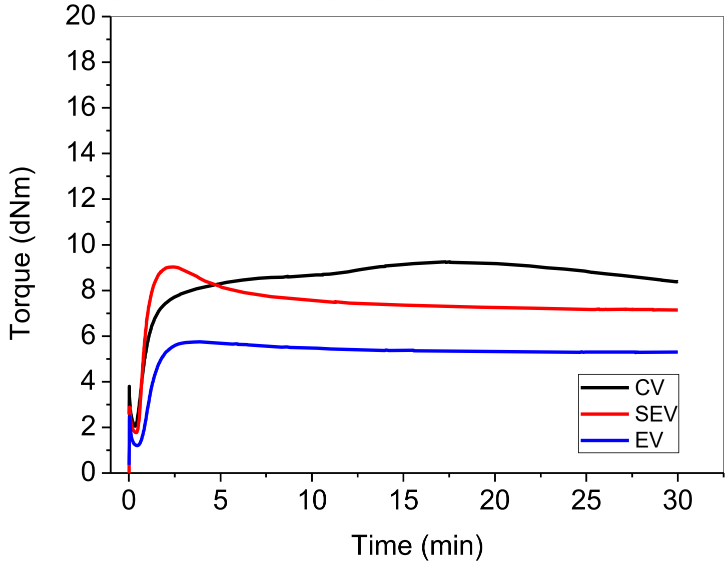

Fig. 4.4. Rheometer curves of ZDBC-accelerated compounds for CV, SEV and EV systems

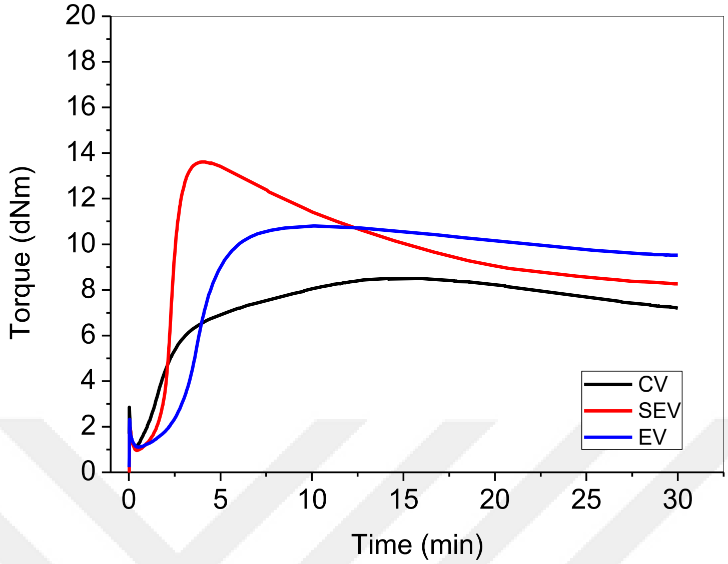

Fig 4.5. Rheometer curves of DETU-accelerated compounds for CV, SEV and EV systems

In order to see the how the different cure systems effect cure the curves (which are presented in Figures 4.1-4.5 for different accelerators), Figures 4.6-4.8 are used as an easier way to compare the cure system effect.

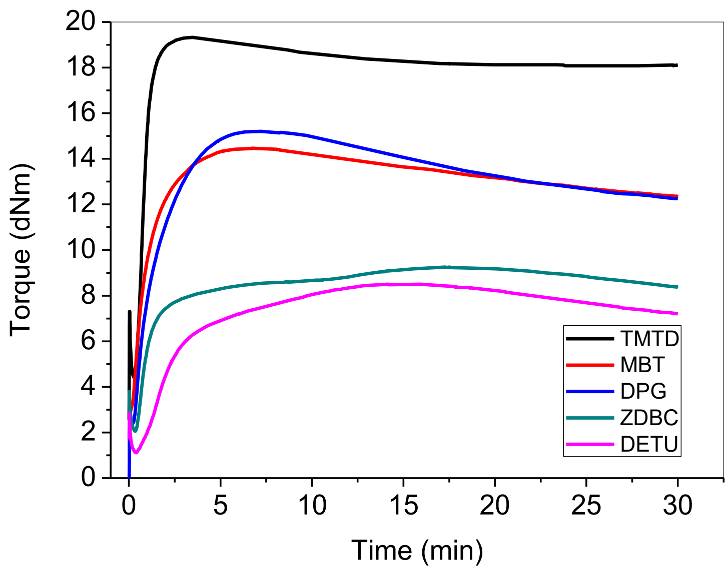

Fig. 4.6. Rheometer curves for conventional cure system

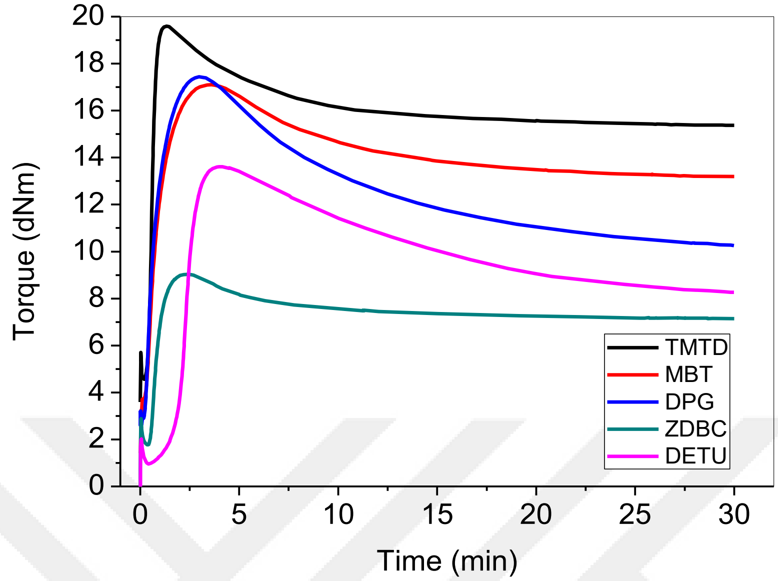

Fig. 4.7. Rheometer curves for semi-efficient cure system

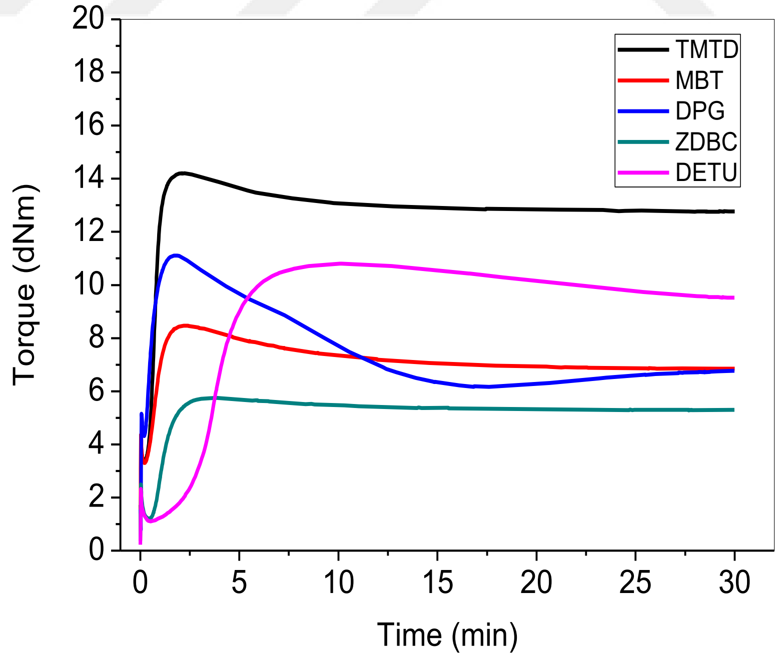

Fig. 4.8. Rheometer curves for efficient cure system

Vulcanization systems have proven to effect cure properties of the vulcanizates and this effect is still a research topic [58, 59].

Considering the reversion phenomena, which normally can happen especially in natural rubber based formulations and when the cure temperature is high enough, we can conclude that the reversion phenomena has the highest attitude in semi-efficient system compared to two other vulcanization systems. There are many studies going on to clarify accelerator type and accelerator to sulfur ration on reversion [58, 60, 61]. Our results show that compounds prepared with the conventional vulcanization system show the least reversion tendency. In addition, we can conclude that the reversion attitude increases with the decrease in cure rate. The vulcanizates containing fast group accelerators show better reversion resistance compared to vulcanizates containing moderate and slow accelerator groups.

M_L, M_H, ts_2, t_{90}, cure extent and cure rate index values of the TMTD, MBT, DPG, ZDBC and DETU-accelerated compounds for different vulcanization systems are listed in Table 4.1-4.5.

Table 4.1. M_L, M_H, ts_2, t_{90}, cure extent and CRI values of TMTD-accelerated compounds

Accelerator-cure system	M_L(dNm)	M_H(dNm)	t_s2(min)	t_{90}	Cure Extent (dNm)	Cure Rate Index (CRI)
TMTD-CV	2.03	14.46	0.51	1.46	12.43	105.26
TMTD-SEV	2.47	20.66	0.46	0.97	18.19	196.07
TMTD-EV	2.69	14.06	0.49	1.16	11.37	149.25

Table 4.2. ML, MH, ts2, t90, cure extent and CRI values of MBT-accelerated compounds

Accelerator-cure system	M_L(dNm)	M_H(dNm)	t_s2(min)	t_{90}	Cure Extent (dNm)	Cure Rate Index (CRI)
MBT-CV	2.82	14.46	0.36	2.96	11.64	38.46
MBT-SEV	6.08	18.5	0.44	1.78	12.42	74.62
MBT-EV	2.81	7.88	0.71	1.39	5.07	147.06

Table 4.3. M_L, M_H, ts_2, t_{90}, cure extent and CRI values of MBT-accelerated compounds

Accelerator-cure system	M_L(dNm)	M_H(dNm)	t_s2(min)	t_{90}	Cure Extent (dNm)	Cure Rate Index (CRI)
DPG-CV	3.61	15.77	0.52	3.65	12.16	31.95
DPG-SEV	4.75	16.79	0.41	1.79	12.04	72.46
DPG-EV	2.36	10.41	0.37	1.01	8.05	156.25

Table 4.4. M_L, M_H, ts_2, t_{90}, cure extent and CRI values of ZDBC-accelerated compounds

Accelerator-cure system	M_L(dNm)	M_H(dNm)	ts2(min)	t_{90}	Cure Extent (dNm)	Cure Rate Index (CRI)
ZDBC-CV	1.14	5.89	1	1.85	4.75	117.64
ZDBC-SEV	1.77	9.03	0.68	1.39	7.26	140.84
ZDBC-EV	2.06	9.25	0.71	7.1	7.19	15.65

Table 4.5. M_L, M_H, ts_2, t_{90}, cure extent and CRI values of DETU-accelerated compounds

Accelerator-cure system	M_L(dNm)	M_H(dNm)	ts2(min)	t_{90}	Cure Extent (dNm)	Cure Rate Index (CRI)
DETU-CV	1.10	8.02	2.94	5.77	6.92	35.33
DETU-SEV	0.96	13.61	1.85	2.94	12.65	91.74
DETU-EV	1.11	8.5	1.46	8.65	7.39	13.91

As it was mentioned before, semi-efficient system generally has the shorter cure time and high cure extent these properties combined with the observed higher maximum torque values can be considered as a process advantage. However, the enhanced reversion in this cure system could cause serious problems especially when applied to cure large-size final product where both cure and cool down time are longer because of vulcanizate size.

Considering lowest torque (M_L) values, we can see that the stiffness of moderate and slow accelerator containing compounds (MBT and DPG accelerated) is generally higher and therefore they have lower processability compared to fast accelerator-containing compounds (TMTD, ZDBC and DETU accelerated compounds). In addition, for the moderate and slow accelerator containing compounds, semi-efficient vulcanization system has the lowest processability but for the fast accelerator-containing compounds, efficient system has the lowest processability.

Considering highest torque (M_H) values, we can see that the TMTD-accelerated compounds. show the highest torque values and generally all the compunds show higher torque values in semi-efficient vulcanization system (this trend is not true for ZDBC and DETU accelerated compounds).

t_s2 is a time from beginning of the test to the time the torque has increases 2 units above M_L value. This value provides information related to the scorch time as it is described in Section 3.3.2. Despite being in fast group ZDBC and DETU has relatively long scorch times and for the other accelerators scorch times are more and less comparable which brings us to the conclusion that the accelerator type and cure system plays only a small roll in scorch time.

T_{90} is the time from the start of the test, to the point where 90% of the M_H value is reached and analyzing the values we can see that TMTD, MBT and DPG accelerated compounds act according their representative groups when it comes to the cure rate. TMDT is the fastest of all. Another interesting aspect of these results is that categorizing ZDBC and especially DETU accelerator as fast accelerator is not true at least in the case of NR/CR based vulcanizates. In DETU accelerated compound case, t_{90} is the longest for all the groups compared and in the case of efficient vulcanization, system for both ZDBC and DETU accelerated systems, t_{90} is incredibly long. Another way to evaluate the cure rate is to compare the CRI values of the samples. Here we can see the results correlate with t_{90} results so that the sorter the t_{90}, the higher is the cure rate index.

For all of the “so called” fast accelerators the semi-efficient system has the highest CRI but for the other groups CRI increases with the accelerator amount. As it can be seen in Figure 4.9, ZDBC and DETU’s CRI values are well below the expected values, since these accelerators are grouped as fast accelerators.

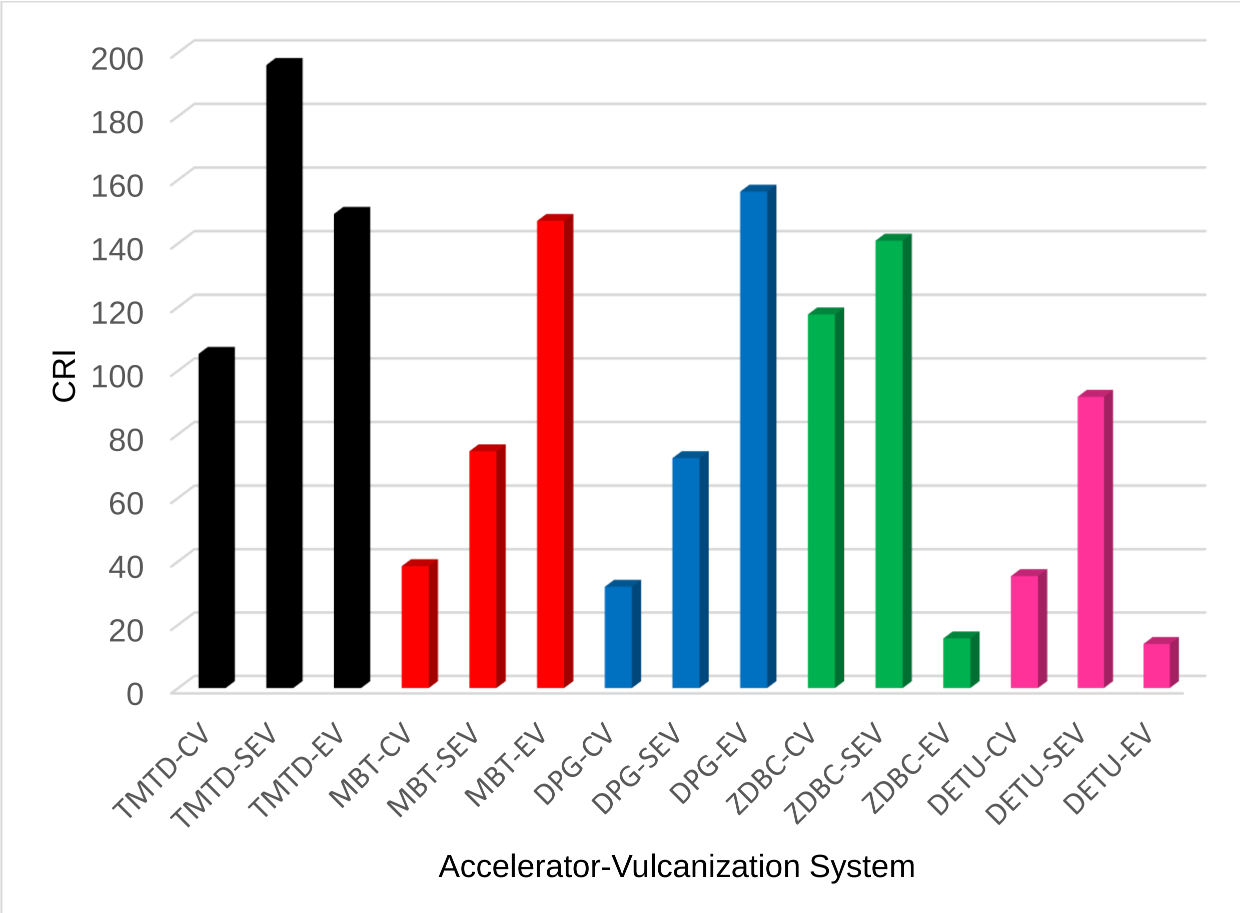

Fig. 4.9. Cure rate index values for all of the prepared compounds

Comparing the cure extent, we can see that when it comes to crosslinking ZDBC accelerator has the worst and TMTD has the best performance between all of the accelerators. Generally, semi-efficient system has the best performance among all when it comes to forming chemical crosslinks. Figure 4.10 is a brief summary and comparison of cure extent values.

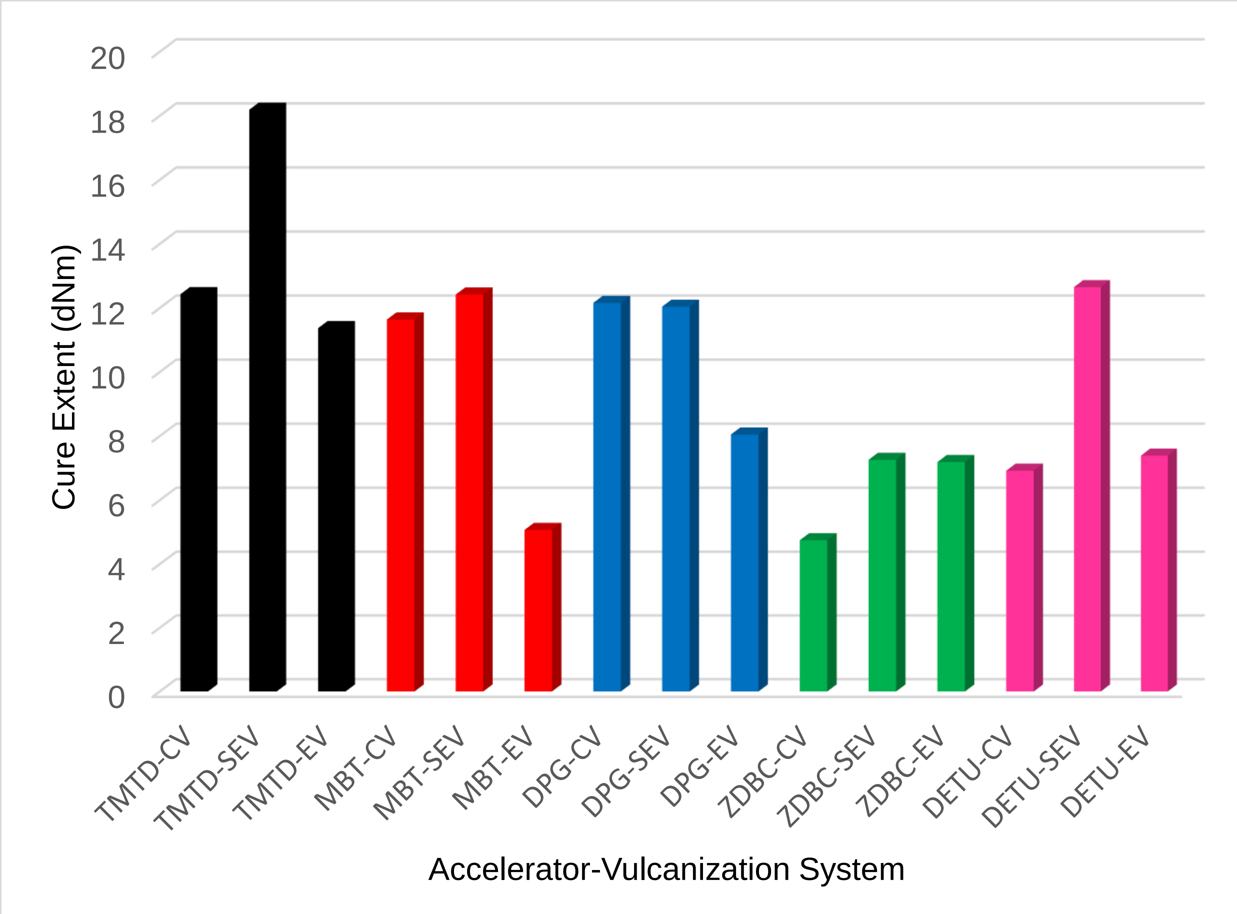

Fig. 4.10. Cure extent values for all of the prepared compounds

From these results, it can be concluded that ZDBC and DETU accelerators do not show a regular and ordered cure kinetics like the other accelerators.

DETU can be used as an efficient accelerator in order to accelerate vulcanization process of chloroprene rubber, since it can act as a sulfur donor, after removing the allylic hydrogen bonded to chlorine atom of chloroprene rubber by using the sulfur atom, which is present in its structure as a way of forming mono sulfidic crosslinks. Since this reaction thought to be the primary reaction at the beginning of vulcanization, the overall cure rate would be very slow and the present amount of DETU mainly consumed in this reaction.

In the case of ZDBC use, it seems that the overall crosslinking needs more energy concentration. The free sulfur needs to warm up and when the crosslinking began it goes on with an acceptable rate.

Comparing the vulcanization systems, it can be concluded that:

- SEV system has the highest cure rate and cure extent however has the poorest reversion resistance.
- Counting out ZDBC and DETU and comparing CV and EV systems, CV system has better cure extent while EV system has better cure rate.

Comparing the accelerators, it can be concluded that:

- TMTD has the highest cure rate and cure extent and lowest reversion rate.
- Cure rate extent follows the pattern of TMTD>MBT>DPG.
- Reversion resistance is higher for fast group accelerators.
- ZDBC and DETU have different cure kinetics and we have to consider this fact while comparing the accelerators.

4.2. Effect of Accelerator Type and Cure Systems on Mechanical Properties of NR/CR Vulcanizates

Mechanical properties have been evaluated after curing of all compounds at hot press in 170°C and cure times according to rhemmeter results. Then all the samples stored at room temperature for 24 hours before mechanical test been carried out according to ASTM D412-16 standard. Each test has been repeated for at least five times and the results are average values. Figures 4.11-4.15 show strain-stress curves of TMTD, MBT, DPG, ZDBC and DETU-accelerated vulcanizates.

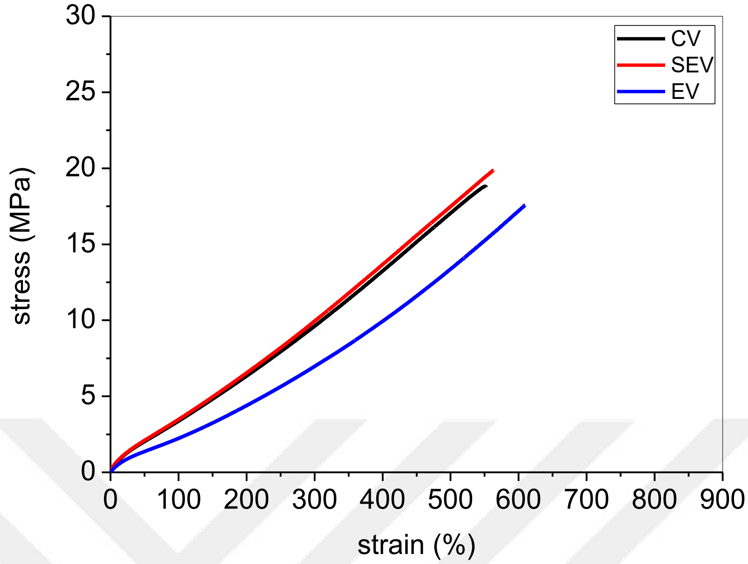

Fig. 4.11. Strain-stress curves for TMTD-accelerated vulcanizate cured using CV, SEV and EV systems

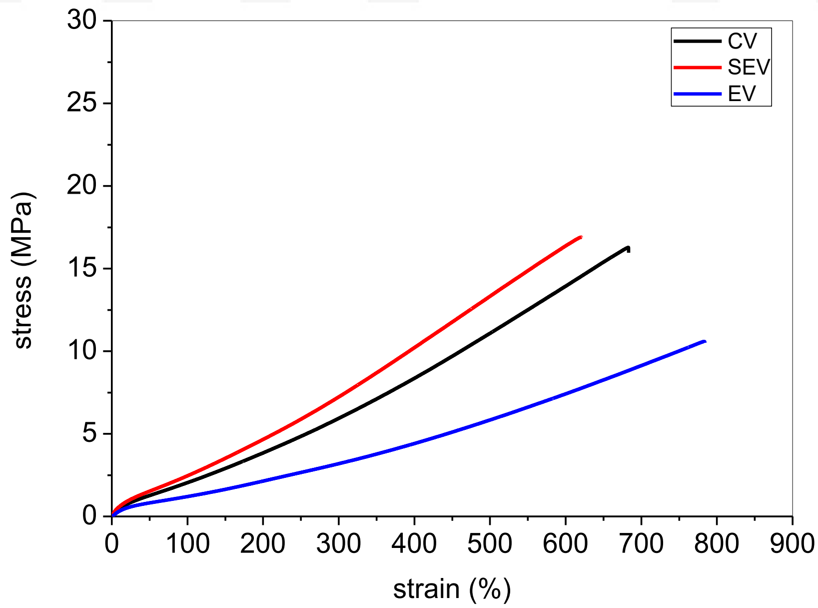

Fig. 4.12. Strain-stress curves for MBT-accelerated vulcanizate cured using CV, SEV and EV systems

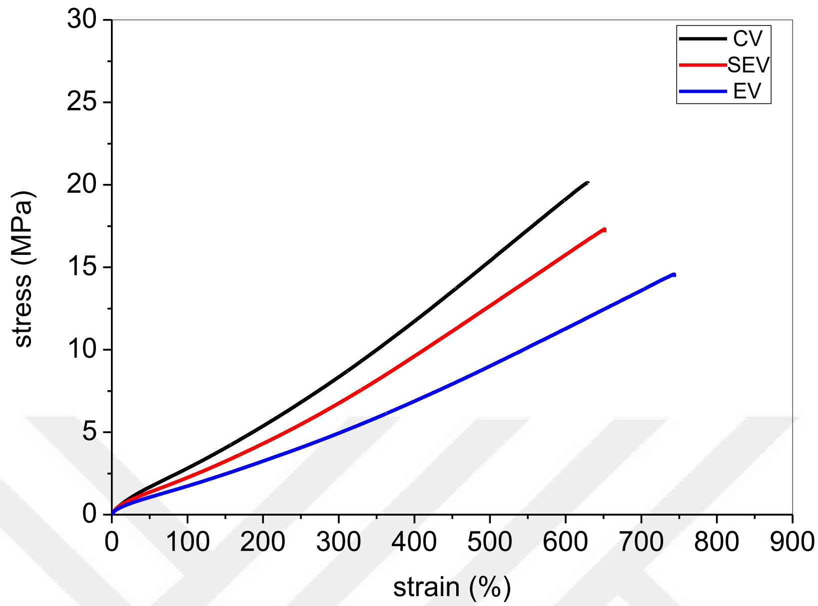

Fig. 4.13. Strain-stress curves for DPG-accelerated vulcanizate cured using CV, SEV and EV systems

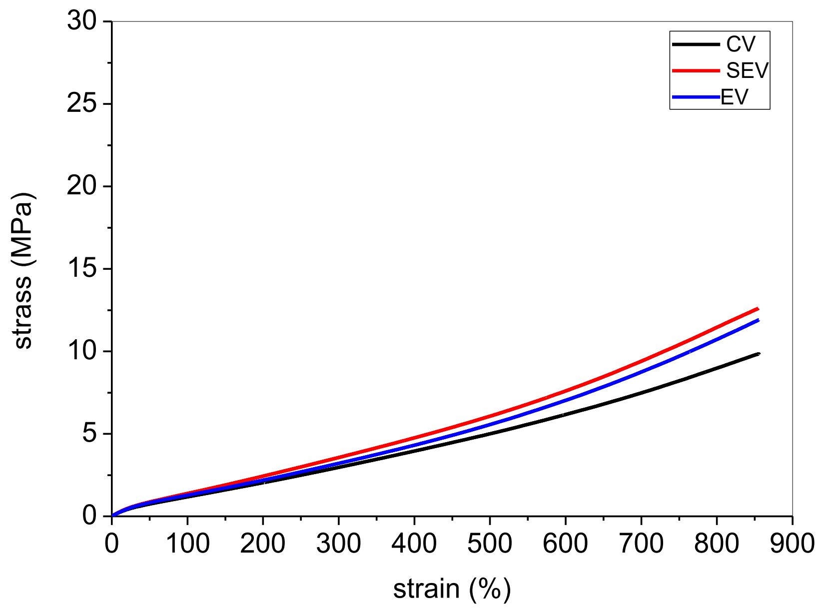

Fig. 4.14. Strain-stress curves for ZDBC-accelerated vulcanizate cured using CV, SEV and EV systems

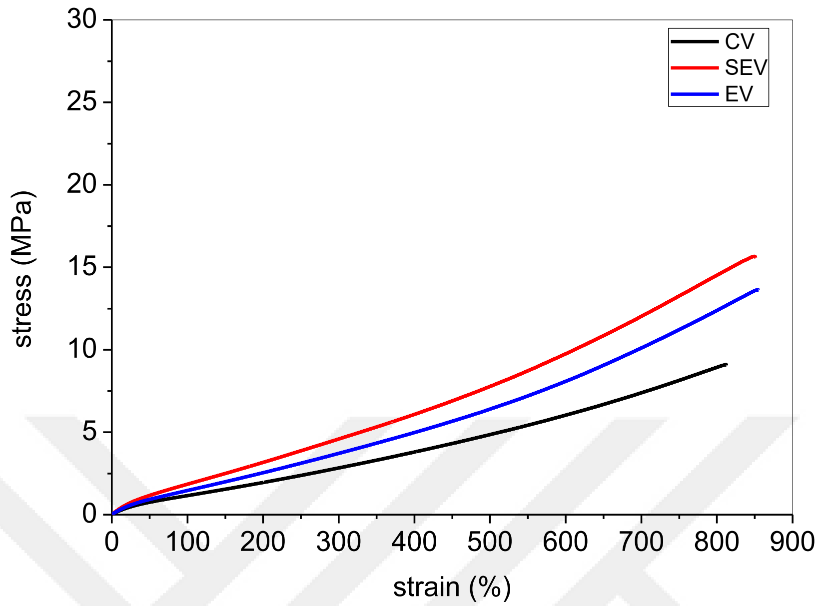

Fig. 4.15. Strain-stress curves for DETU-accelerated vulcanizate cured using CV, SEV and EV systems

In other to see the effect of vulcanization system on the vulcanizate mechanical properties, the pre-presented curves (Figures 4.11-4.15) have been redrawn in a way to show the vulcanization system effect, which are presented in Figures 4.16-4.18.

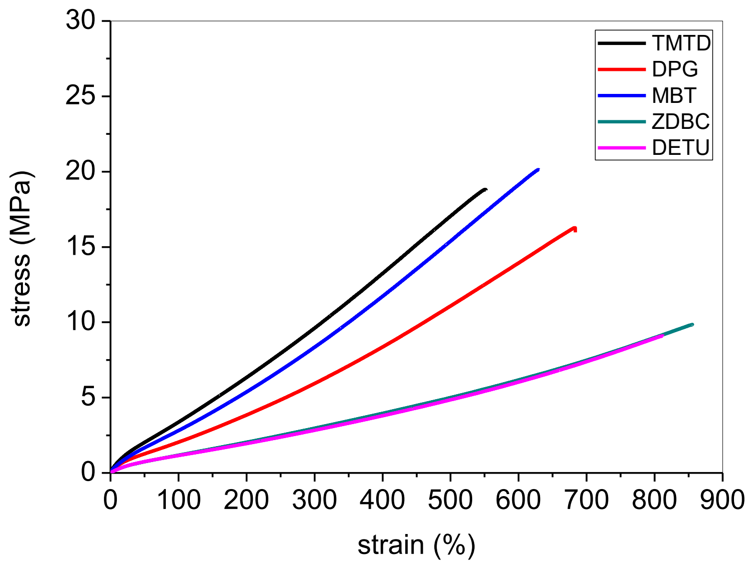

Fig. 4.16. Strain-stress curves for the conventional vulcanization system

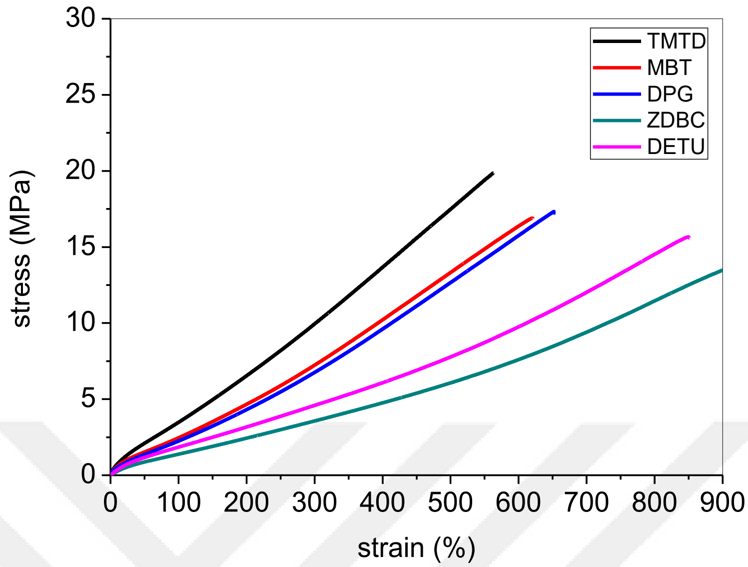

Fig. 4.17. Strain-stress curves for the semi-efficient vulcanization system

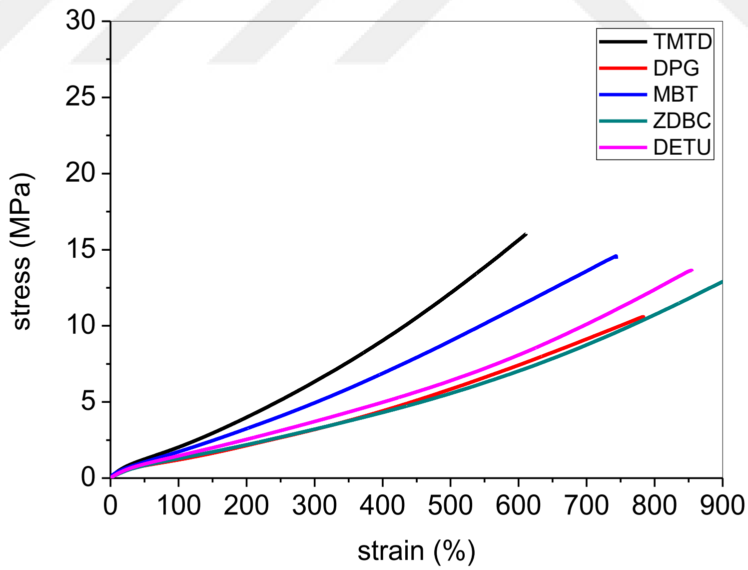

Fig. 4.18. Strain-stress curves for the efficient vulcanization system

Tensile strength and elongation at break values have been presented in Tables 4.6-4.10 for TMTD, MBT, DPG, ZDBC and DETU-accelerated vulcanizates respectively. Table 4.11 shows initial modulus and modulus values at 100 and 300% strain. Initial modulus which is a measure of elasticity and is dependent to crosslink density of the elastomers, is the slope of strain-stress curve in the elastic deformation (initial) region of the curve.

Table 4.6. Tensile strength and elongation at break values for TMTD-accelerated vulcanizates

	Tensile strength (MPa)	Elongation at break (%)
Conventional vulcanization (CV)	18.3	549
Semi-efficient vulcanization (SEV)	19.9	563
Efficient vulcanization (EV)	17.3	610

Table 4.7. Tensile strength and elongation at break values for MBT-accelerated vulcanizates

	Tensile strength (MPa)	Elongation at break (%)
Conventional vulcanization (CV)	16.6	690
Semi-efficient vulcanization (SEV)	16.9	620
Efficient vulcanization (EV)	10.8	783

Table 4.8. Tensile strength and elongation at break values for DPG-accelerated vulcanizates

	Tensile strength (MPa)	Elongation at break (%)
Conventional vulcanization (CV)	17.8	609.6
Semi-efficient vulcanization (SEV)	17.1	651.9
Efficient vulcanization (EV)	14.9	760.2

Table 4.9. Tensile strength and elongation at break values for ZDBC-accelerated vulcanizates

	Tensile strength (MPa)	Elongation at break (%)
Conventional vulcanization (CV)	10.4	871
Semi-efficient vulcanization (SEV)	13.2	855
Efficient vulcanization (EV)	13.2	856

Table 4.10. Tensile strength and elongation at break values for DETU-accelerated vulcanizates

	Tensile strength (MPa)	Elongation at break (%)
Conventional vulcanization (CV)	8.7	805
Semi-efficient vulcanization (SEV)	15.0	852
Efficient vulcanization (EV)	13.5	860

Table 4.11. Initial modulus and modulus values at 100 and 300% strain for different accelerators cured using CV, SEV and EV systems.

	Initial Modulus			Modulus at 100% strain			Modulus at 300% strain		
	CV	SEV	EV	CV	SEV	EV	CV	SEV	EV
TMTD	9.97	11.20	5.49	2.81	3.18	1.42	3.64	3.75	1.89
MBT	8.59	11.90	7.35	1.60	2.01	1.04	2.15	2.66	1.44
DPG	7.44	10.40	7.84	1.80	2.03	1.30	2.51	2.67	1.57
ZDBC	2.61	2.94	1.71	0.89	1.04	0.85	0.98	1.15	1.05
DETU	2.60	3.53	3.04	0.78	1.29	1.00	0.92	1.40	1.16

As it can be seen from Table 4.11, SEV system has the highest elastic modulus between the vulcanization systems. TMTD accelerator has the highest elastic modulus value and ZDBC and DETU seems to have significantly low elastic modulus values.

Figure 4.19 is a brief comparison of tensile strength values of different vulcanizates.

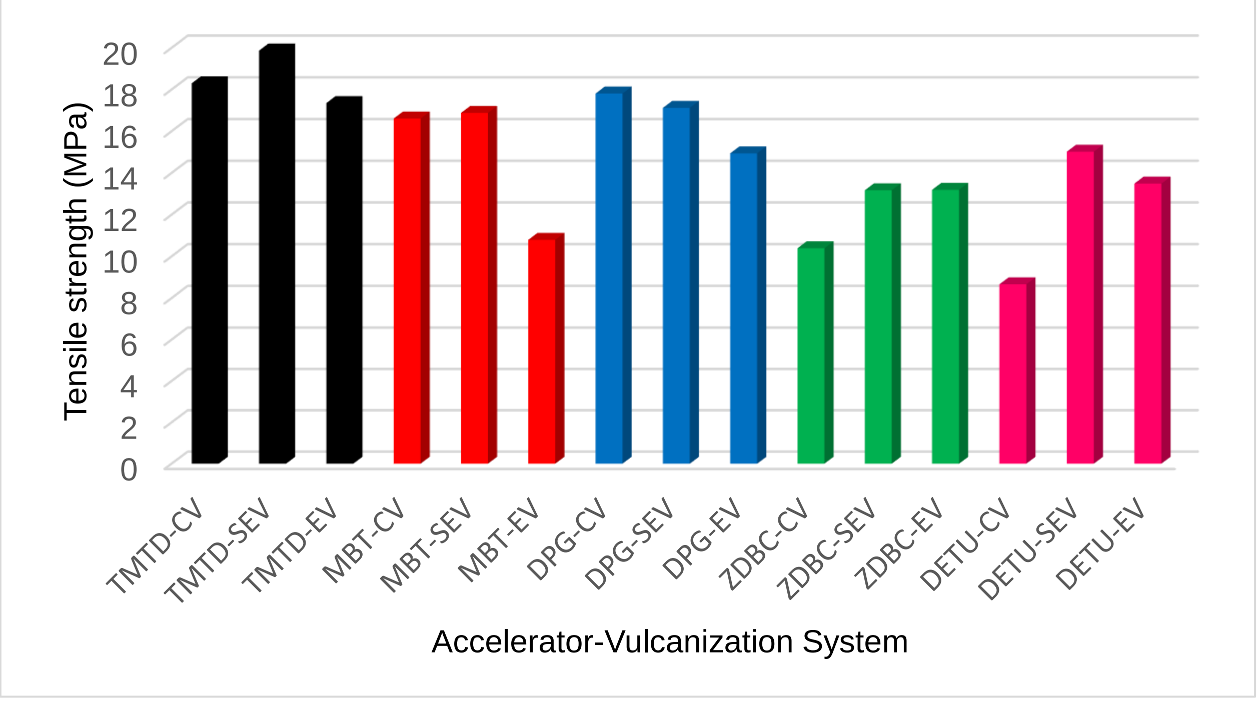

Fig. 4.19. Tensile strength values for all of the prepared compounds

As it can be seen from the Figures and Tables, mechanical properties of the vulcanizates strongly depend on the accelerating capacity (very fast, fast, of slow) of the vulcanization system used. Besides, accelerator class has an important effect on the mechanical properties, even accelerating capacities of the used accelerator are the same.

For instance, in conventional vulcanization system, elongation at break values of the vulcanizates decrease while tensile strength values have a considerable increase for higher accelerating capacity (TMTD>MBT>DPG). In other words, the present order gives lower elastic modulus. It would like to remind that, for the same formulations, state of cure values were quite closed to each other in their respective cure curves. Similar mechanical properties for TMTD, MBT, and DPG – accelerated conventional vulcanization may be attributed to closed and considerably higher cure extents. When TMTD and ZDBC, which have similar cure rates, are compared to each other, ZDBC-accelerated vulcanizates have poorer mechanical properties. This is most likely about lower cure extent values for ZDBC. ZDBC and DETU-accelerated vulcanizates exhibit similar mechanical properties due to quite closed cure extents, related to closed crosslink densities.

Nearly all of the accelerators show the best performance when the semi-efficient vulcanization system has been applied for cure. TMTD-accelerated shows the overall best performance. MBT and DPG-accelerated vulcanizates exhibit similar performance when the semi-efficient vulcanization system has been applied but the performance of DPG-accelerated vulcanizate falls with the decrease of sulfur amount (efficient vulcanization system).

Variation in crosslink density of an elastomeric system manifests itself especially on tensile modulus. Variation can also be followed by monitoring elongation at break values. Here, elongation at break values should be evaluated considering accelerator type for all the vulcanization system.

When it comes to comparison between the elongation values of different accelerators and systems, it can be easily seen that as it was expected, there is generally a reverse inter-dependence between elongation at break and tensile strength values for more and less all the vulcanizates. The vulcanizates containing accelerators with higher cure efficiency has higher elongation. Figure 4.20 shows the elongation values of different accelerator containing vulcanizates for three different vulcanization system.

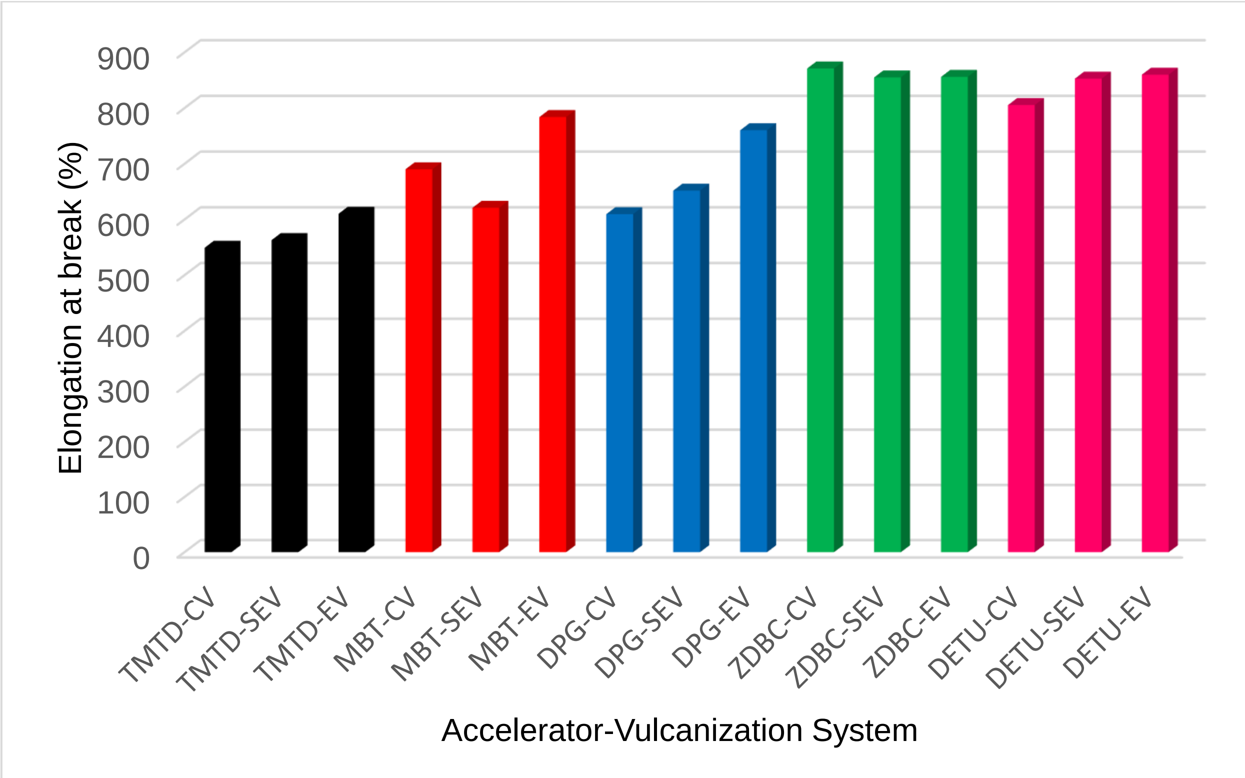

Fig. 4.20. Elongation at break values for all of the prepared compounds

For conventional vulcanization system, mechanical test results are all in good agreement with what is predicted according to cure extent values resulted from MDR test presented in section 4.1. The accelerators and systems with higher cure rate and cure extent values (cure efficiency) show higher elongation.

For efficient vulcanization system, TMTD-accelerated vulcanizate have higher elongation, whereas its cure extent is higher than that of MBT and DPG-accelerated vulcanizates. Because, elongation at break is also closely related to crosslink distribution (mono, di, and polysulfidic) as well as crosslink density. This effect has also been tried to explain by weathering study in the later sections.

Comparing the vulcanization systems, it can be concluded that:

- SEV system has the best mechanical performance.
- Counting out ZDBC and DETU and comparing CV and EV systems, CV system has higher tensile strength

Comparing the accelerators, it can be concluded that:

- TMTD has the best mechanical performance.
- MBT and DPG have quite similar mechanical performance.
- DETU which had good cure extent and acceptable CRI for SEV system, has also acceptable mechanical performance.

4.3. Effect of Accelerator Type and Cure Systems on Crosslink Density of NR/CR Vulcanizates

Crosslink density effectively changes mechanical and aging properties of rubber vulcanizates and literature is full of studies that investigate these effects using different methods to calculate crosslink density [35, 62, 63]. The theoretical background of Pulse NMR has been described in part 3.2.2. The T2 (spin-spin) relaxation parameter of pulse-NMR to characterize of network mobility. The uncured and un-aged compounds have been tested at magnet temperature of 40°C by applying the spin-echo pulse sequence to obtain the free induction decay curves. The FID curves of TMTD, MBT, DPG, ZDBC and DETU-accelerated compounds presented in figures 4.21-4.25, respectively.

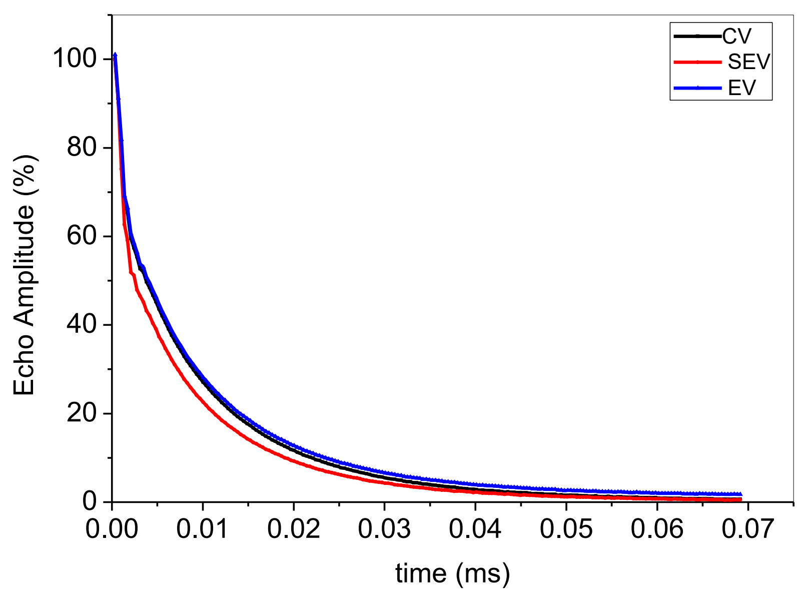

Fig. 4.21. Free induction decay cure for TMTD-accelerated vulcanizate cured using CV, SEV and EV systems

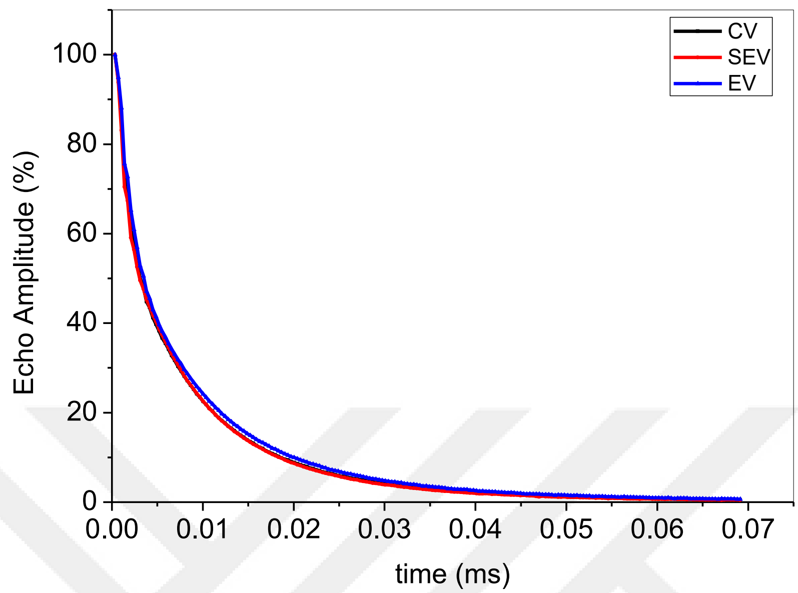

Fig. 4.22. Free induction decay cure for MBT-accelerated vulcanizate cured using CV, SEV and EV systems

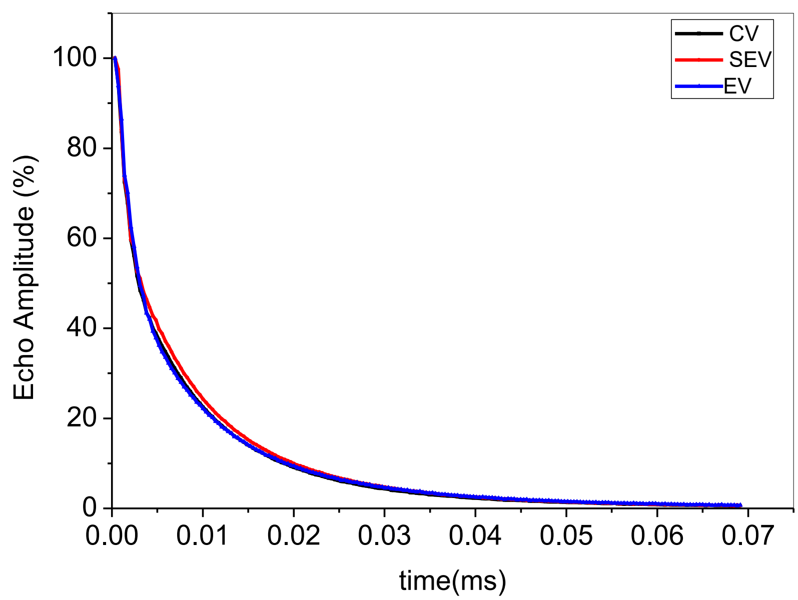

Fig. 4.23. Free induction decay cure for DPG-accelerated vulcanizate cured using CV, SEV and EV systems

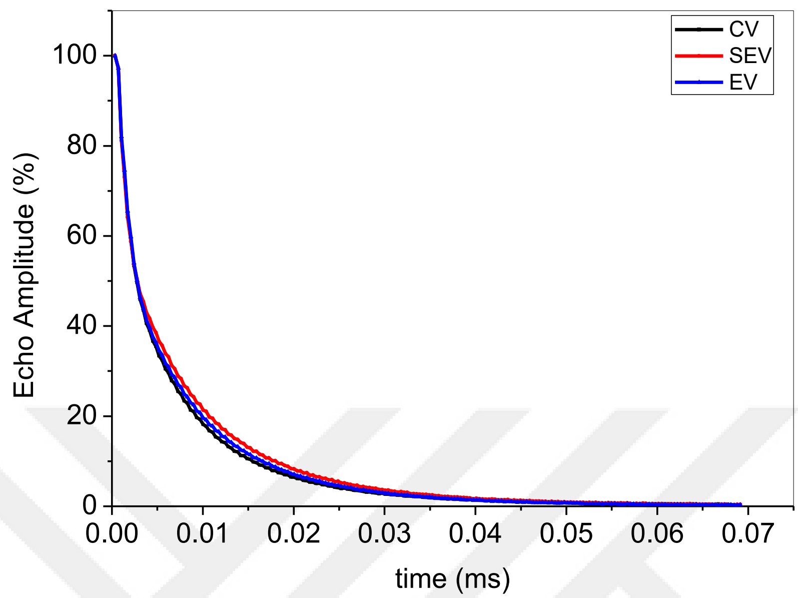

Fig. 4.24. Free induction decay cure for ZDBC-accelerated vulcanizate cured using CV, SEV and EV systems

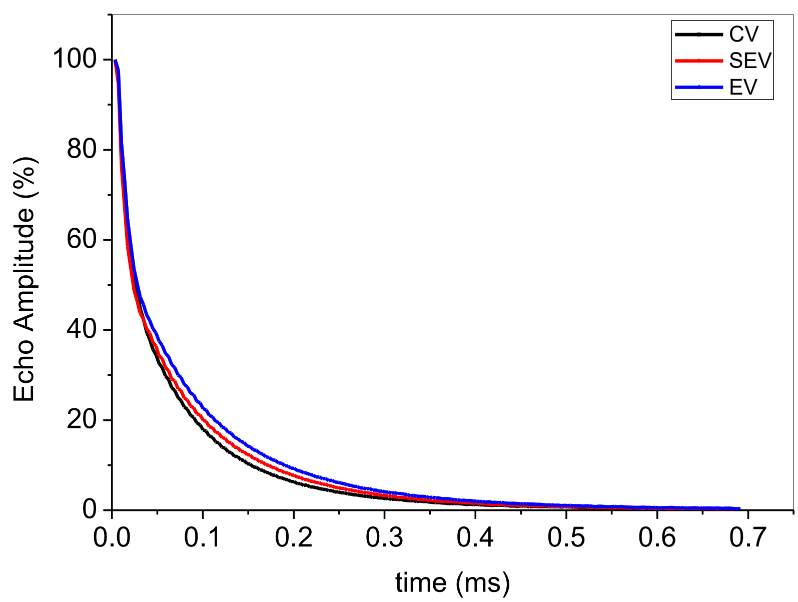

Fig. 4.25. Free induction decay cure for DETU-accelerated vulcanizate cured using CV, SEV and EV systems

In order to see the effect of cure system on FID curves the pre plotted curves (4.19-4.23) have been redrawn to percent cure system effect (Figures 4.26-4.28).

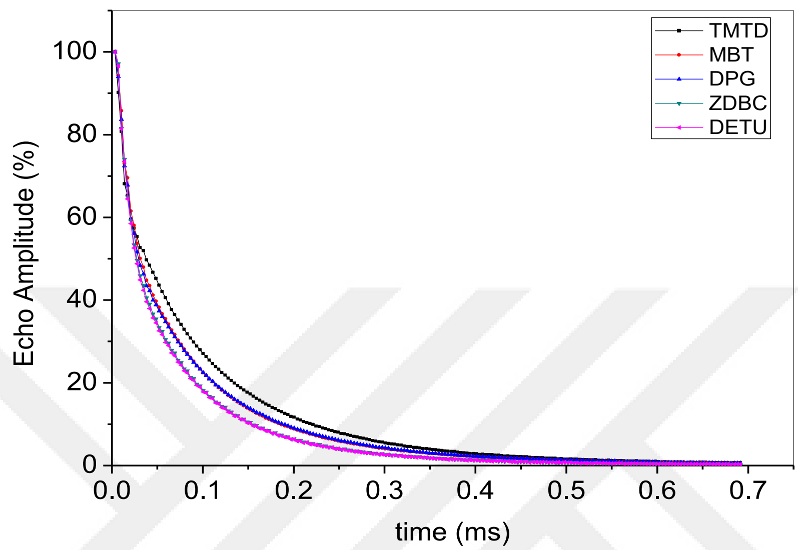

Fig. 4.26. Free induction decay curve for vulcanizates cured using conventional system

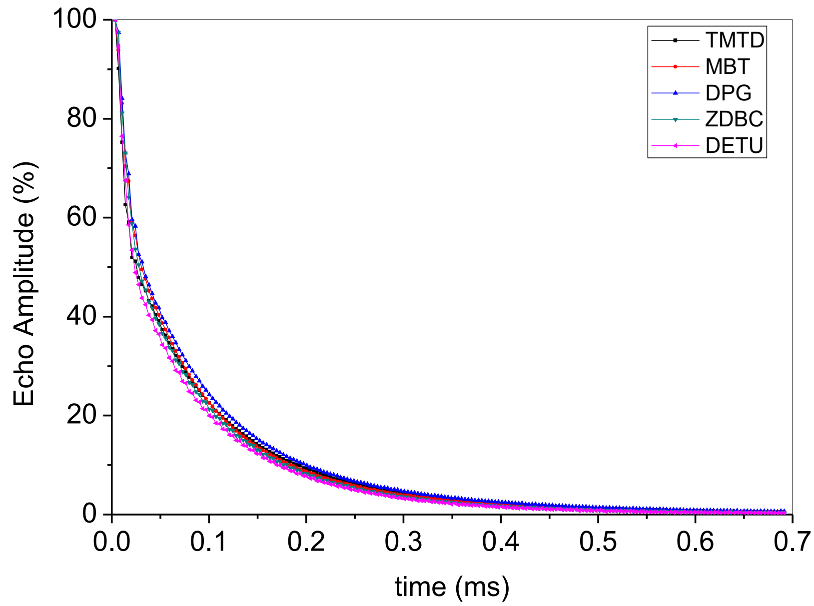

Fig. 4.27. Free induction decay curve for vulcanizates cured using semi-efficient system

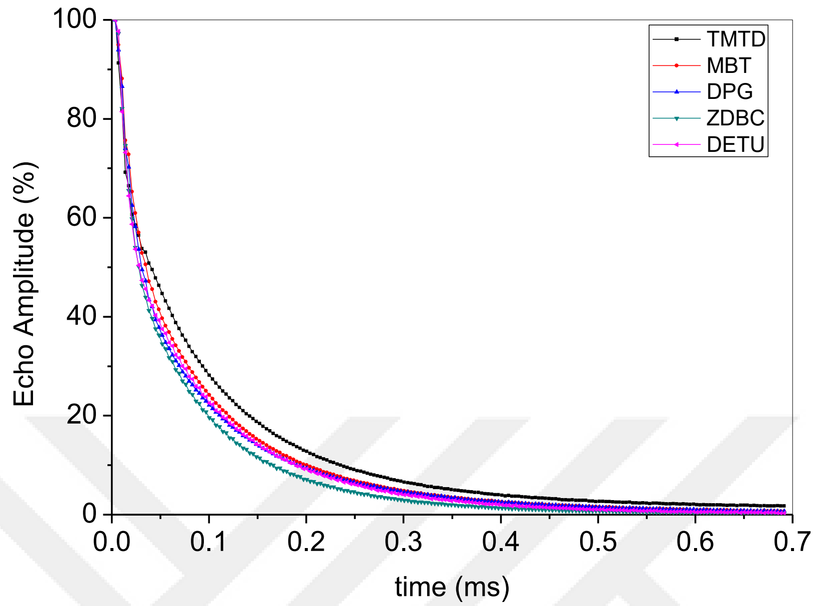

Fig. 4.28. Free induction decay curve for vulcanizates cured using efficient system

After obtaining the FID curves, they have been fitted using OriginLab 8.0 ® and equation 4.1 due to Hahn-Echo-Decay principle [51]

$$M(t) = A*\exp(-t/T - q M_2 t) + B*\exp(-t/T) \tag{4.1}$$

Where M_2 describes intermolecular dipolar interactions determined from line shape analyses ($M_2 = 0.86 *10^{10}$ s^{-2} for NR) [47]. q is a correction factor for fast molecular motion and a measure of restriction in molecular motion, therefore physical and chemical XLD can be calculated using this value. Values of q can vary between 0-1 where q = 0 represents fully isotropic fast motions and q = 1 represents totally rigid polymer chain motions. q value for the uncured compounds have been calculated and named as q_0.

Equation 4.2 [51] has been used to calculate molecular weight between crosslinks.

$$M_c = \frac{3}{5\sqrt{q-q_0}} C_\infty \frac{M_{RU}}{N} \tag{4.2}$$

Where M_c is averaged molecular mass between crosslinks, c is backbone units per Kuhn-segment (7.4 for NR) [51], M_{RU} is the average molar mass of one monomeric units (74.9 for NR/CR 80:20) and N is backbone bonds per monomeric unit (4 for both NR and CR).

Finally, crosslink densities have been calculated by dividing the specific density of samples by the pre-calculated M_c values as shown in equation 4.3.

$$XLD = \rho / M_c \quad (4.3)$$

The calculated q, q_0, M_c and XLD values of the vulcanizates have been presented in Tables 4.12-4.14.

Table 4.12. Motion factor (q), average molecular mass between cross-links (M_c) & crosslinking density (XLD) values of vulcanizates cured using conventional vulcanization system

Accelerator	q	q_0	M_c (g/mol)	XLD (mol/cm^3)
TMTD	5.46E-05	1.95E-05	1.27E+04	1.18E-04
MBT	2.80E-05	1.60E-05	2.18E+04	6.87E-05
DPG	3.09E-05	1.55E-05	1.04E+04	7.82E-05
ZDBC	3.05E-05	1.73E-05	2.08E+04	4.81E-05
DETU	3.04E-05	1.86E-05	2.20E+04	4.55E-05

Table 4.13. Motion factor (q), average molecular mass between cross-links (M_c) and crosslinking density (XLD) values of vulcanizates cured using semi-efficient vulcanization system

Accelerator	q	q_0	M_c (g/mol)	XLD (mol/cm^3)
TMTD	8.21E-05	1.79E-05	9.42E+03	1.59E-04
MBT	4.54E-05	1.80E-05	1.44E+04	1.04E-04
DPG	4.13E-05	1.70E-05	1.53E+04	9.78E-05
ZDBC	3.99E-05	1.75E-05	1.59E+04	9.41E-05
DETU	5.48E-05	1.67E-05	1.22E+04	1.23E-04

Table 4.14. Motion factor (q), average molecular mass between cross-links (M_c) and crosslinking density (XLD) values of vulcanizates cured using efficient vulcanization system

Accelerator	q	q_0	M_c (g/mol)	XLD (mol/cm^3)
TMTD	4.70E-05	1.93E-05	1.44E+04	1.04E-04
MBT	2.39E-05	1.82E-05	3.18E+04	4.71E-05
DPG	2.30E-05	1.77E-05	3.29E+04	4.56E-05
ZDBC	3.14E-05	1.71E-05	2.00E+04	7.50E-05
DETU	4.04E-05	1.75E-05	1.58E+04	9.51E-05

The XLD values for all of the prepared vulcanizates have been presented in figure 4.29 to provide easy comparison between all the results.

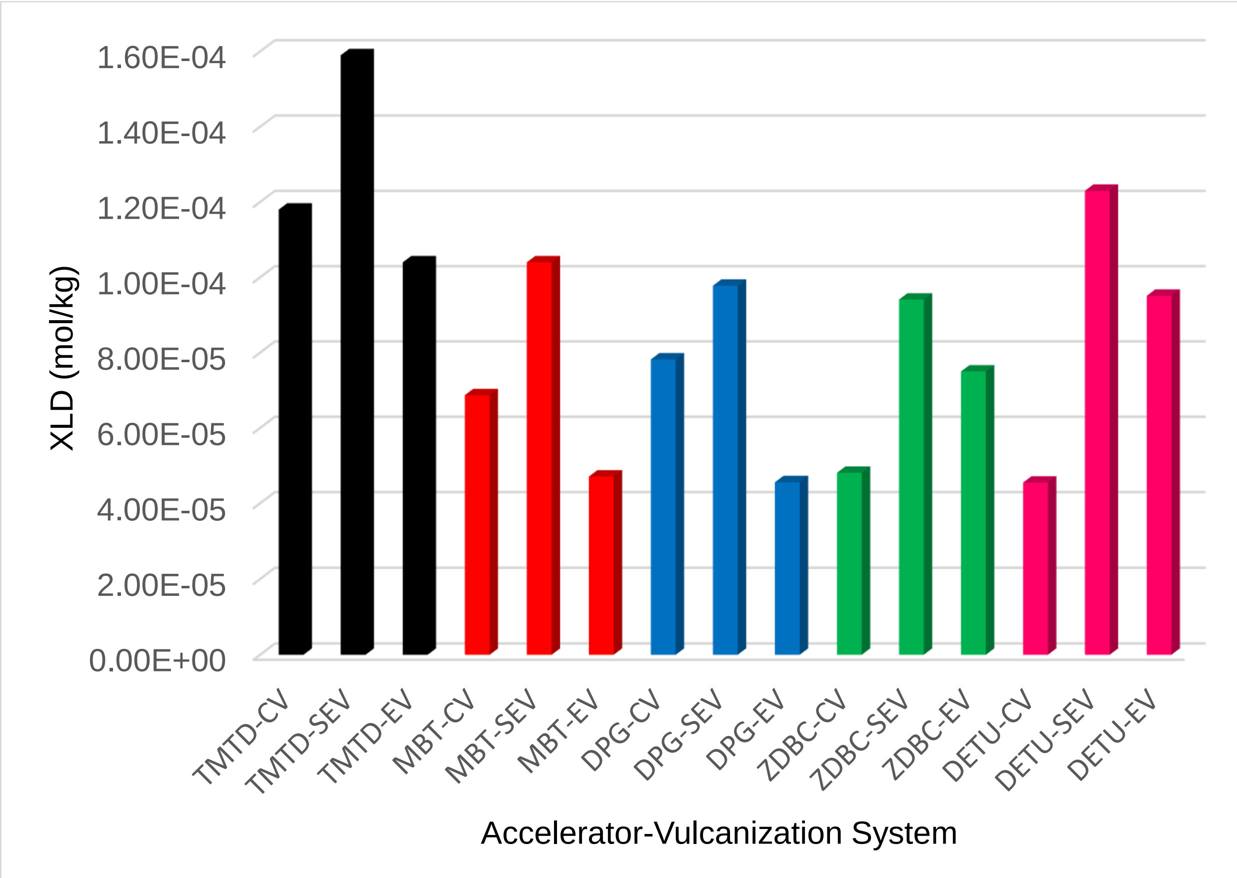

Fig. 4.29. XLD values for all of the prepared vulcanizates

As it can be seen, both accelerator type and cure system have significant effect on crosslink density of the vulcanizates. TMTD-accelerated vulcanizate exhibits the highest crosslink density while all the accelerators show their highest XLD value when cured using semi-efficient system. ZDBC and DETU accelerators show higher XLD when cured with efficient vulcanization system compared to conventional system. The results are in agreement with cure extent and mechanical properties.

As it has been mentioned in section 3.6.1, polymer scientists and especially engineers tend to consider cure index as a measure of crosslink density since the determination of exact XLD requires time (when swelling experiments is performed) or special instruments (like pulse NMR). Therefore, we have tried to cross-check the results and see how closely these values are related to each other. Figure 4.30 is the presentation of this comparison.

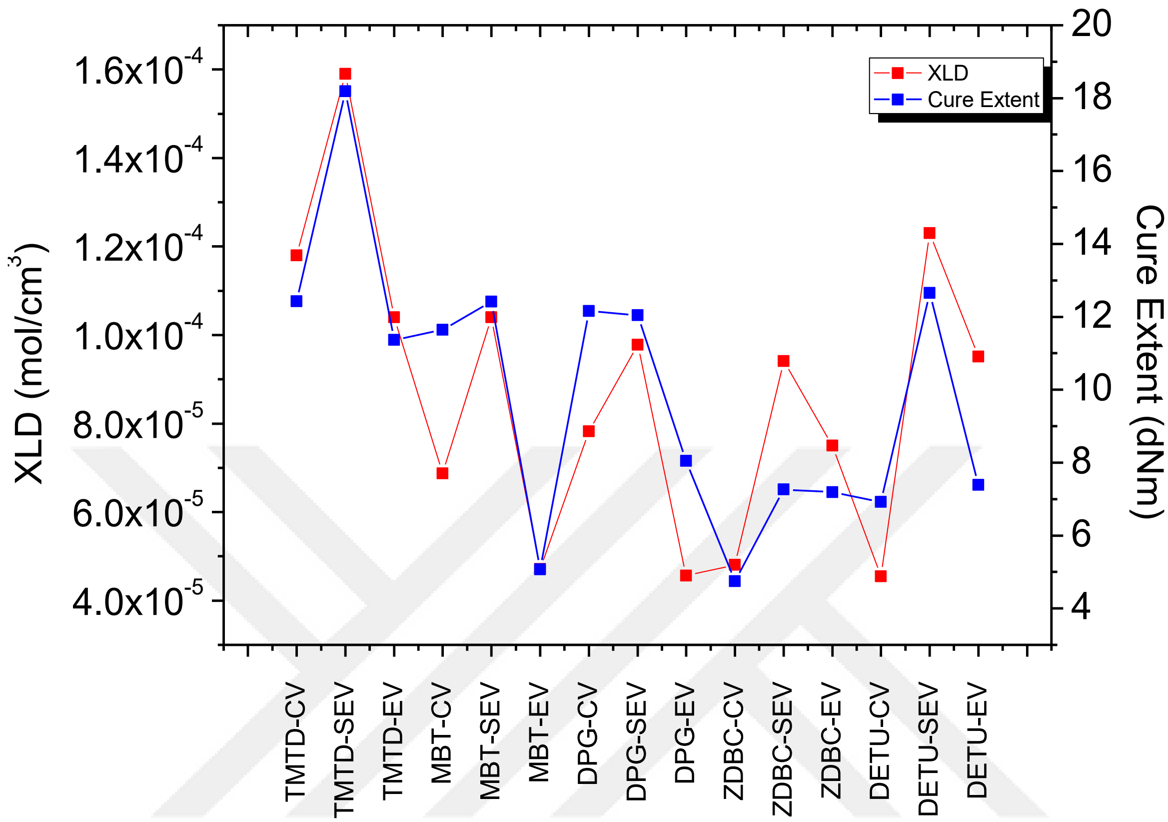

Fig. 4.30. XLD calculated by pulse NMR vs. cure extent calculated by rheometer

As it can be seen from the Figure 2.28, there is a good inter dependence at most parts of the graph. The most interesting findings on the correlation of crosslink density and cure extent values stand out for MBT in CV and ZDBC in SEV. For the compound MBT-CV, crosslink density value is quite low than expected from the rheological properties. It is well known that, MBT has a limited solubility especially in NR. This is a more dominant problem in case of high sulfur loadings due to competing vulcanization reactions by the accelerator and sulfur in rubber matrix. For conventional system, much higher sulfur content is considered when compared to SEV and EV systems. Therefore, difference between two properties (XLD and cure extent) is much more significant for MBT-accelerated CV system. For ZDBC-accelerated vulcanizates, it is clearly seen from the Figure 4.30 that, there is not a systematic trend in difference between the aforementioned results. This may be attributed to uncontrollable interest of ZDBC in the complex vulcanization reaction media and different dispersion states of two rubbers in the compounds. ZDBC has similar solubilities in both rubbers (NR and CR); but also it is more active in CR vulcanization as other zinc containing accelerators.

Comparing the vulcanization systems, it can be concluded that:

- SEV system has the highest XLD.
- Counting out ZDBC and DETU and comparing CV and EV systems, CV system has higher XLD.

Comparing the accelerators, it can be concluded that:

- TMTD has the highest XLD.
- DETU has quite high XLD values especially for SEV system.

4.4. Effect of Accelerator Type and Cure Systems on Temperature Scanning Stress Relaxation Behavior of NR/CR Vulcanizates

As it was mentioned in section 3.6.3, TSSR method is a new method of analyzing structural differences of elastomers since these structural differences can completely change stress relaxation behavior of the rubber vulcanizates. In the scope on this thesis, TSSR method has been applied to NR/CR vulcanizates to find out how accelerator type and vulcanization system can change stress relaxation pattern of the vulcanizates and how can it be related to the structural differences such as crosslink type and density. The test has been carried out according to the method described in section 3.6.3 and using the machinery introduced in section 3.3.4.

Stress relaxation curves of the TMTD, MBT, DPG, ZDBC and DETU-accelerated vulcanizates have been presented in Figures 4.31-4.35 respectively.

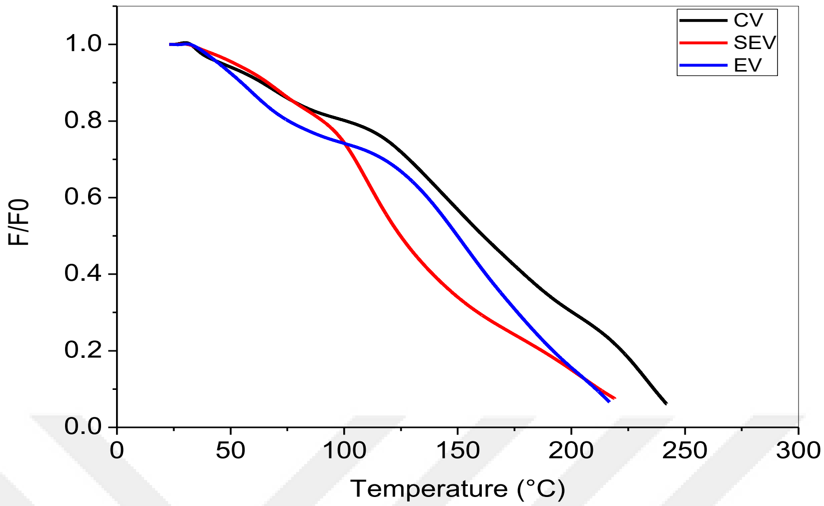

Fig. 4.31. Anisothermal relaxation curves for TMTD-accelerated vulcanizates cured using CV, SEV and EV systems

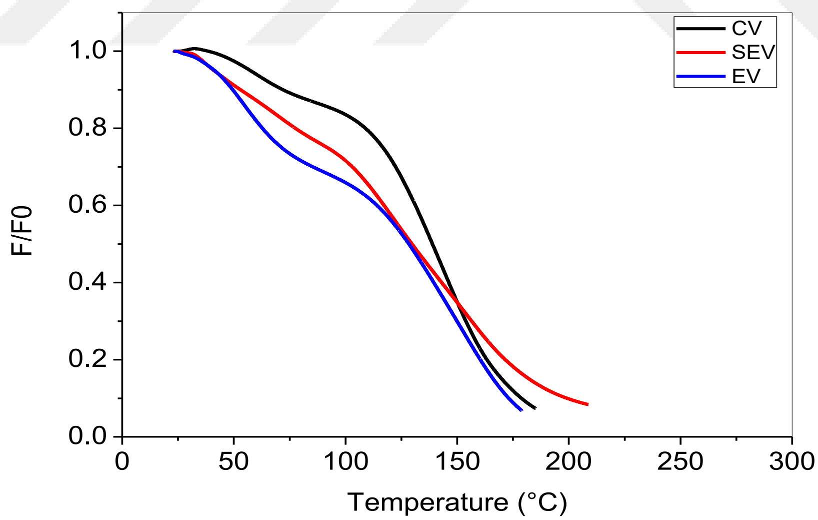

Fig.4.32. Anisothermal relaxation curves for MBT-accelerated vulcanizates cured using CV, SEV and EV systems

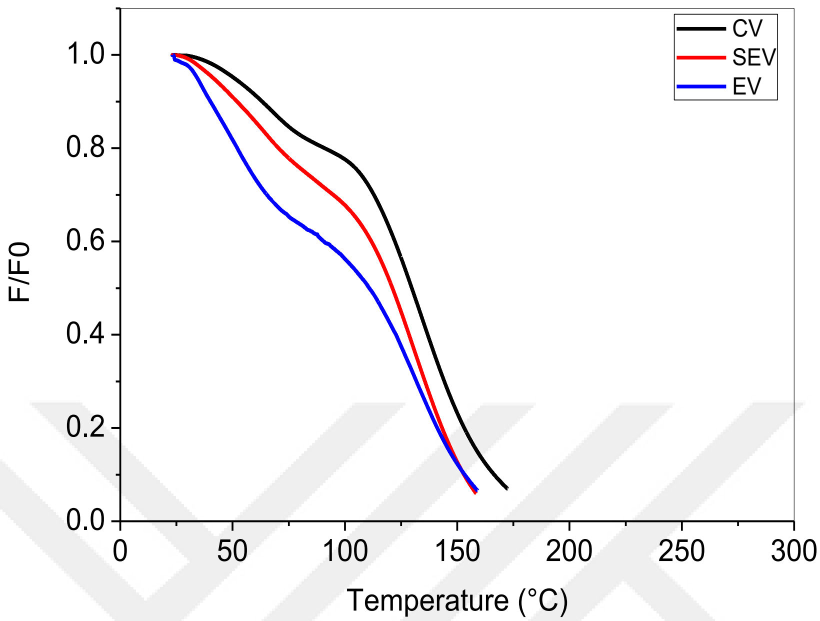

Fig.4.33. Anisothermal relaxation curves for DPG-accelerated vulcanizates cured using CV, SEV and EV systems

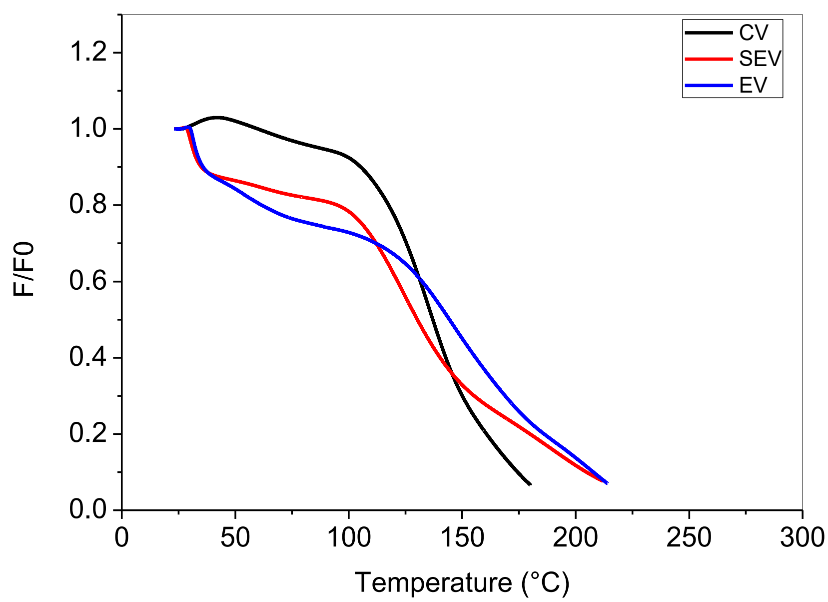

Fig.4.34. Anisothermal relaxation curves for ZDBC-accelerated vulcanizates cured using CV, SEV and EV systems

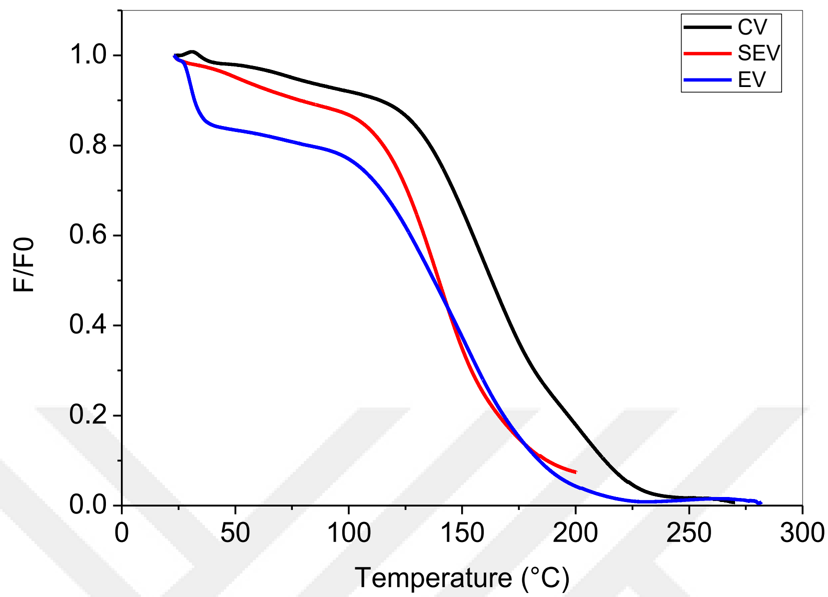

Fig. 4.35. Anisothermal relaxation curves for DETU-accelerated vulcanizates cured using CV, SEV and EV systems

In order to observe the accelerator related relaxation change, Figures 4.36-4.38 were plotted to show stress relaxation curves of the different accelerators cured using conventional, semi efficient and efficient vulcanization systems, respectively.

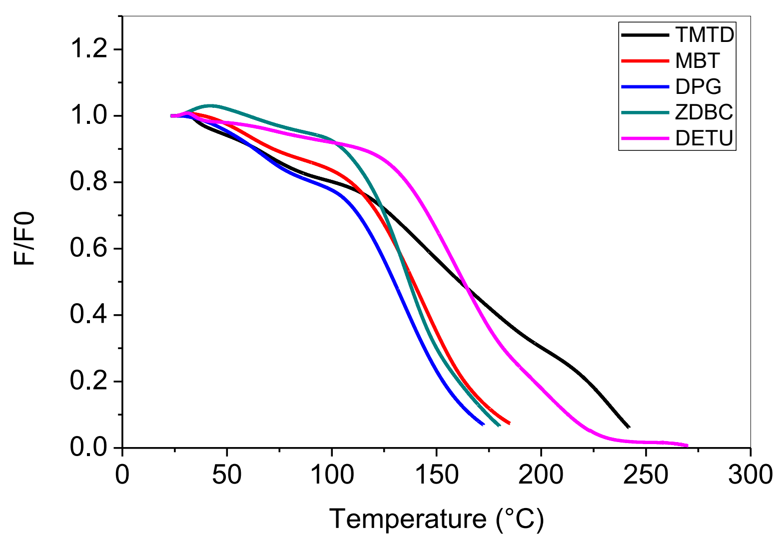

Fig.4.36. Anisothermal relaxation curves for conventional vulcanization system

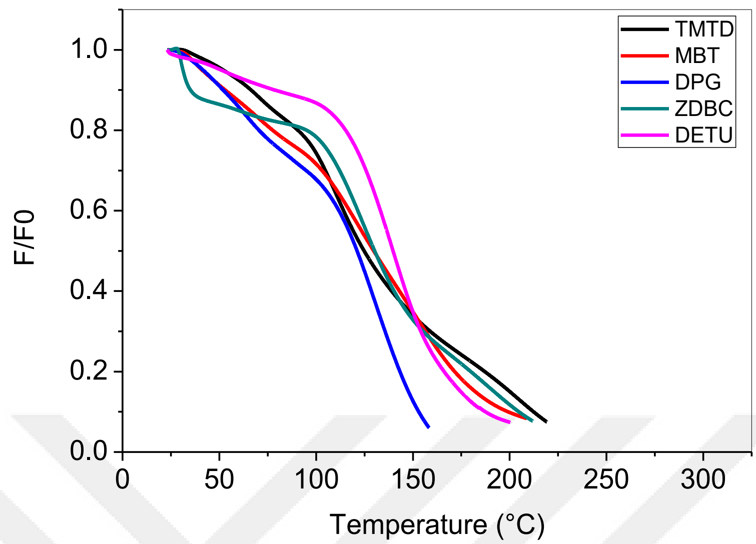

Fig.4.37. Anisothermal relaxation curves for semi-efficient vulcanization system

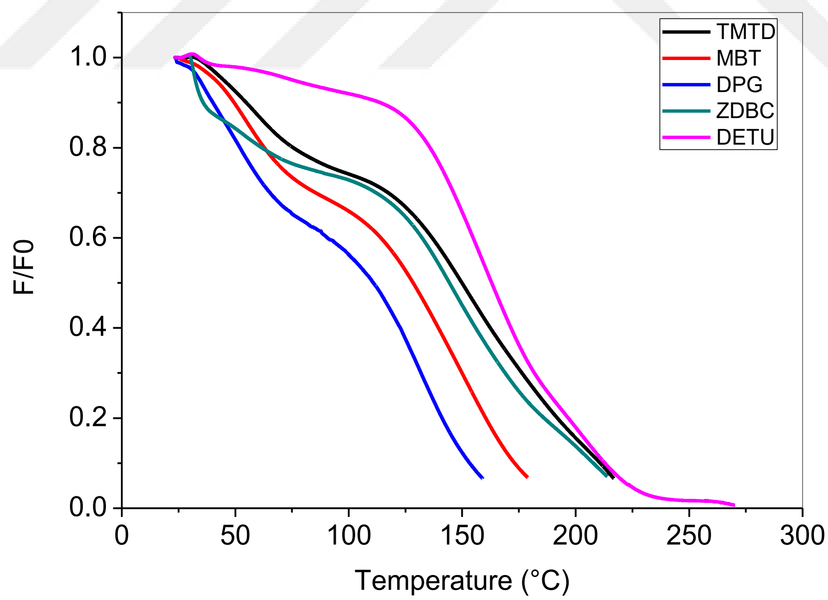

Fig.4.38. Anisothermal relaxation curves for efficient vulcanization system

When the comparison is made between TMTD, MBT and DPG accelerated vulcanizates we can see that the accelerators with lower cure efficiency exhibit stronger stress decrease behavior. Despite the fact that ZDBC and DETU accelerated vulcanizates exhibit completely different behaviors due to their different cure characteristics (section

4.1) this stress general behavior pattern is also true for them. Since the accelerators with higher cure eficency also show better reversion resistance (section 4.1) this behavior thought to be related to the higher ratio of polysulfidic crosslinks in fast cured vulcanizate when compared to two other accelerator groups. Polysulfidic crosslinks consume some of thermal energy to form mono and disulfidic crosslinks so the exhibit delayed reversion and stress decrease. The obtained TSSR test data have been listed in Tables 4.15-4.19.

Table 4.15. TSSR analysis data for TMTD-accelerated vulcanizates

	σ_0 (MPa)	T_{10} (°C)	T_{50} (°C)	T_{90} (°C)	TSSR Index
Conventional vulcanization (CV)	0.82	64.0	161.3	236.4	0.63
Semi-efficient vulcanization (SEV)	1.27	66.4	124.8	212.3	0.60
Efficient vulcanization (EV)	0.99	54.9	149.9	210.8	0.60

Table 4.16. TSSR analysis data for MBT-accelerated vulcanizates

	σ_0 (MPa)	T_{10} (°C)	T_{50} (°C)	T_{90} (°C)	TSSR Index
Conventional vulcanization (CV)	0.67	72.0	139.0	178.8	0.71
Semi-efficient vulcanization (SEV)	1.14	53.0	129.8	199.2	0.59
Efficient vulcanization (EV)	0.39	49.5	128.4	173.1	0.63

Table 4.17. TSSR analysis data for DPG-accelerated vulcanizates

	σ_0 (MPa)	T_{10} (°C)	T_{50} (°C)	T_{90} (°C)	TSSR Index
Conventional vulcanization (CV)	0.85	63.2	129.8	166.5	0.69
Semi-efficient vulcanization (SEV)	0.84	52.0	121.2	153.0	0.67
Efficient vulcanization (EV)	0.50	40.2	110.9	153.3	0.59

Table 4.18. TSSR analysis data for ZDBC-accelerated vulcanizates

	σ_0 (MPa)	T_{10} (°C)	T_{50} (°C)	T_{90} (°C)	TSSR Index
Conventional vulcanization (CV)	0.53	78.6	139.8	187.5	0.70
Semi-efficient vulcanization (SEV)	0.85	32.1	137.6	184.0	0.65
Efficient vulcanization (EV)	0.61	113.9	163.0	212.9	0.69

Table 4.19. TSSR analysis data for DETU-accelerated vulcanizates

	σ_0 (MPa)	T_{10} (°C)	T_{50} (°C)	T_{90} (°C)	TSSR Index
Conventional vulcanization (CV)	0.52	105.3	137.1	174.4	0.76
Semi-efficient vulcanization (SEV)	0.79	35.1	130.3	204.7	0.60
Efficient vulcanization (EV)	0.52	35.9	144.4	207.8	0.59

For all of the vulcanizates, temperatures above 110°C are very critical since thermal resistance of NR and CR is around this temperature, and reversion starts at temperatures around 140°C as discussed before.

DETU and ZDBC accelerated vulcanizates show a plateau at 75-125°C in their stress relaxation curves (Figure 4.34-4.35). This behavior is despite the fact that temperature resistance for NR and CR rubbers is at 100 and 120°C, respectively therefore a stress decrease is expected in this region. However, as described in section 4.1 cure kinetics and efficacy of these two accelerators is quite different from the other three types.

Comparing the initial stress (σ_0) values shows that there is an interdependence between the XLD and σ_0 when both systems and accelerators concerned. Initial stress is higher for the vulcanizates with higher XLD values.

The results indicates that nearly for all vulcanizates, TSSR index follows the CV>SEV>EV order when comparison made among different vulcanization systems. This can be related to the same order in fatigue resistance, which was discussed in part 2.7.1. Higher ratio of polysulfidic crosslinks in CV cured vulcanizates seems to be the reason behind this order.

Comparing the T_{90} values sometimes referred to as maximum service temperature, one could conclude that the vulcanizates prepared using fast group accelerator show higher maximum service temperatures. This can be related to overall higher crosslinking density combined with higher ratio of polysulfidic crosslinks in fast accelerator containing vulcanizates.

Comparing the vulcanization systems, it can be concluded that:

- CV system has the best and EV has the worst relaxation performance.
- CV system has the highest service temperature.

Comparing the accelerators, it can be concluded that:

- Fast accelerators have better relaxation performance
- Like mentioned before ZDBC and DETU seem to have delayed vulcanization.

4.5. Effect of Weathering on Mechanical Properties of NR/CR Vulcanizates

The weathering of the prepared vulcanizates have been carried out according to ASTM G 154-cycle 7 standard. One standard cycle consists of 8 hours of UV irradiation, 3 h and 45 min of condensation followed by 45 min of water spray. After the samples taken out of the accelerated weathering machine, they have been stored at room temperature before mechanical test have been carried out. The test has been carried out according to exactly the same standard and conditions for the unaged samples. Each sample have been tested at least for five times and the given values are averages. Figure 4.36 is a representative strain-stress test result. These curves obtained for TMTD-accelerated vulcanizates after different weathering periods. The complete test results for each vulcanization system have been given in tables 4.20-4.22. Retention values, which are used as an easy way to get an idea about the attitude of weathering, have been obtained from equation 4.3

$$\text{Retention \%} = \frac{Value\ after\ aging}{Value\ before\ aging}\ 100 \qquad (4.3)$$

Retention of tensile strength and elongation at break have been calculated for each vulcanizate after each weathering period.

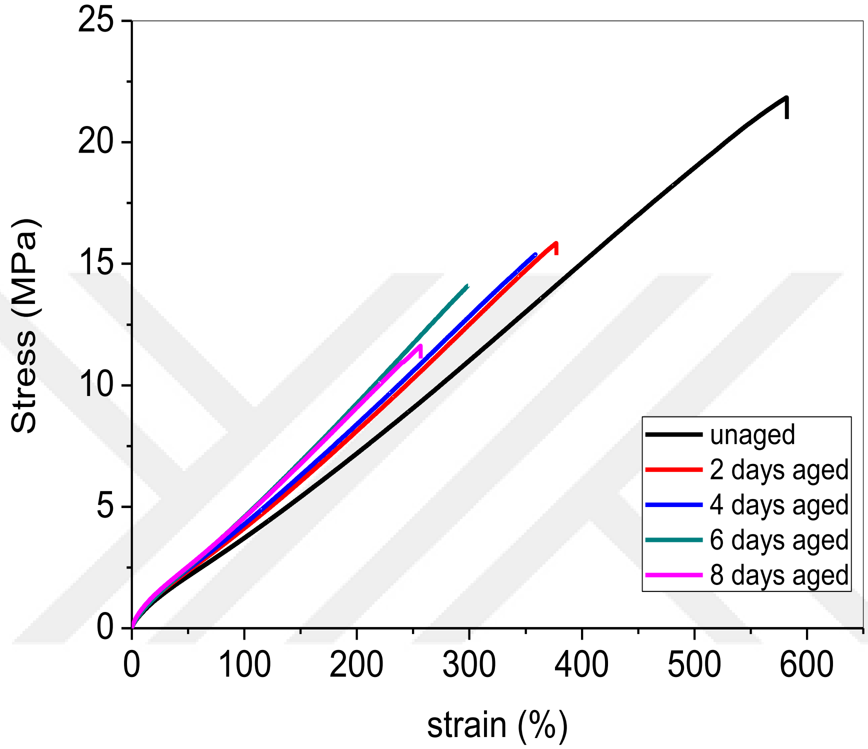

Fig. 4.39. Strain-stress curves of TMTD-accelerated vulcanizates cured using SEV system after different weathering periods

Figure 4.39 has been given as a representative for strain-stress curves of the vulcanizates after different periods of accelerated weathering.

Table 4.20. Tensile strength, elongation at break and retention values of these properties for CV system

Accelerator	Weathering Time (days)	0	2	4	6	8
TMTD	Tensile strength (Mpa)	21.13	18.95	18.23	17.15	16.96
TMTD	Elongation at break (%)	589	511	507	487	484
TMTD	Retention of tensile strength (%)	100	89	86	81	80
TMTD	Retention of Elongation (%)	100	86.69	86	86	82
MBT	Tensile strength (Mpa)	15.44	14.76	14.68	14.52	14.49
MBT	Elongation at break (%)	670	647	632	620	615
MBT	Retention of tensile strength (%)	100	95	95	94	93
MBT	Retention of Elongation (%)	100	96	94	92	91
DPG	Tensile strength (Mpa)	15.82	15.40	15.36	15.21	14.96
DPG	Elongation at break (%)	626	601	587	579	554
DPG	Retention of tensile strength (%)	100	97	97	96	94
DPG	Retention of Elongation (%)	100	96	94	92	88
ZDBC	Tensile strength (Mpa)	10.39	9.17	9.19	8.75	8.71
ZDBC	Elongation at break (%)	871	791	743	702	667
ZDBC	Retention of tensile strength (%)	100	88	88	84	83
ZDBC	Retention of Elongation (%)	100	91	85	80	77
DETU	Tensile strength (Mpa)	9.39	9.18	9.16	9.01	8.720
DETU	Elongation at break (%)	815	813	798	766	720
DETU	Retention of tensile strength (%)	100	98	97	96	93
DETU	Retention of Elongation (%)	100	99	98	94	88

Figures 4.40 and 4.41 show retention values of tensile strength and elongation at break for vulcanizates cured using conventional vulcanization system respectively.

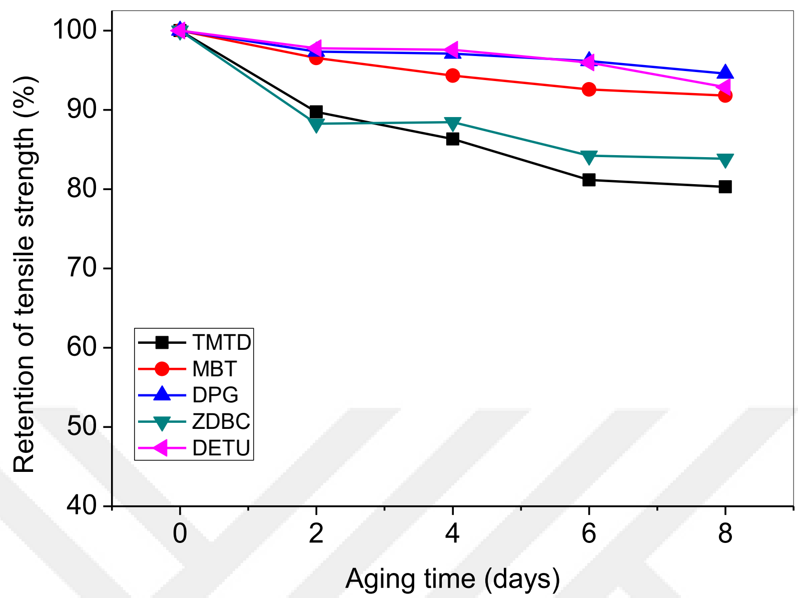

Fig. 4.40. Retention of tensile strength after weathering for CV system

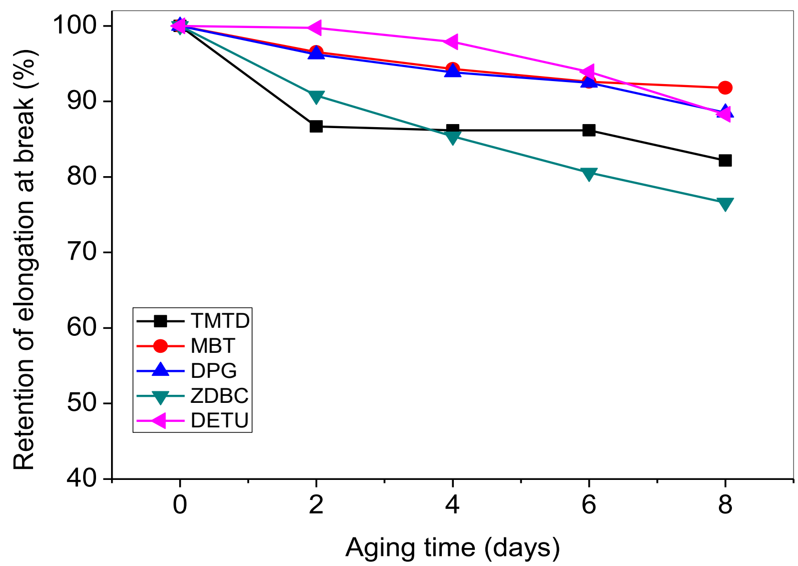

Fig. 4.41. Retention of elongation at break after weathering for CV system

Table 4.21. Tensile strength, elongation at break and retention values of these properties for SEV system

Accelerator	Weathering time (days)	0	2	4	6	8
TMTD	Tensile strength (MPa)	20.59	15.44	15.19	13.87	11.54
TMTD	Elongation at break (%)	582	381	369	310	254
TMTD	Retention of tensile strength (%)	100	75	74	67	56
TMTD	Retention of elongation (%)	100	65	63	53	43
MBT	Tensile strength (MPa)	16.18	16.10	16.08	15.61	15.52
MBT	Elongation at break (%)	520	513	508	483	476
MBT	Retention of tensile strength (%)	100	99	99	96	95
MBT	Retention of elongation (%)	100	98	97	92	91
DPG	Tensile strength (MPa)	18.41	16.97	16.88	16.70	15.41
DPG	Elongation at break (%)	681	669	594	564	449
DPG	Retention of tensile strength (%)	100	92	91	90	84
DPG	Retention of elongation (%)	100	98	87	83	66
ZDBC	Tensile strength (MPa)	13.17	12.60	10.30	9.58	6.98
ZDBC	Elongation at break (%)	907	772	646	575	463
ZDBC	Retention of tensile strength (%)	100	95	78	72	52
ZDBC	Retention of elongation (%)	100	85	71	63	51
DETU	Tensile strength (MPa)	15.02	14.76	13.98	12.93	12.69
DETU	Elongation at break (%)	852	833	787	755	730
DETU	Retention of tensile strength (%)	100	98	93	86	84
DETU	Retention of elongation (%)	100	98	92	89	85

Figures 4.42 and 4.43 show retention values of tensile strength and elongation at break for vulcanizates cured using semi-efficient vulcanization system respectively.

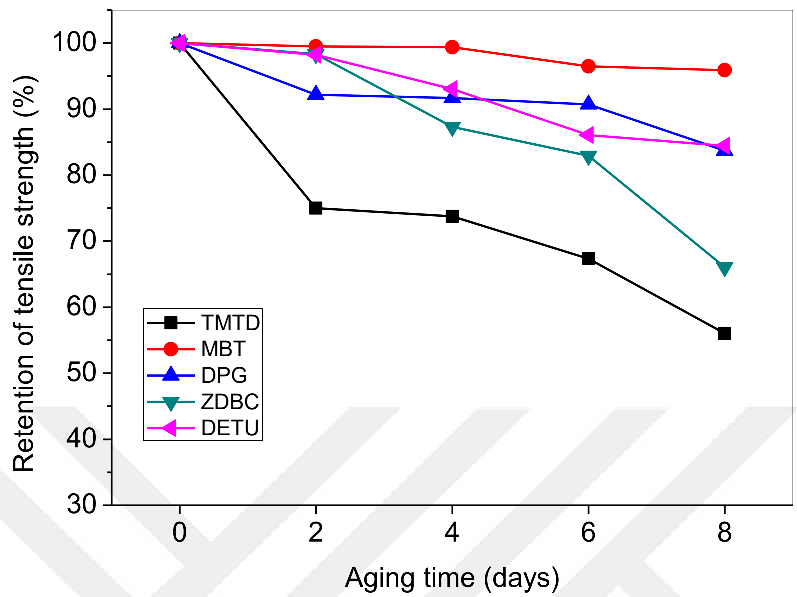

Fig. 4.42. Retention of tensile strength after weathering for SEV system

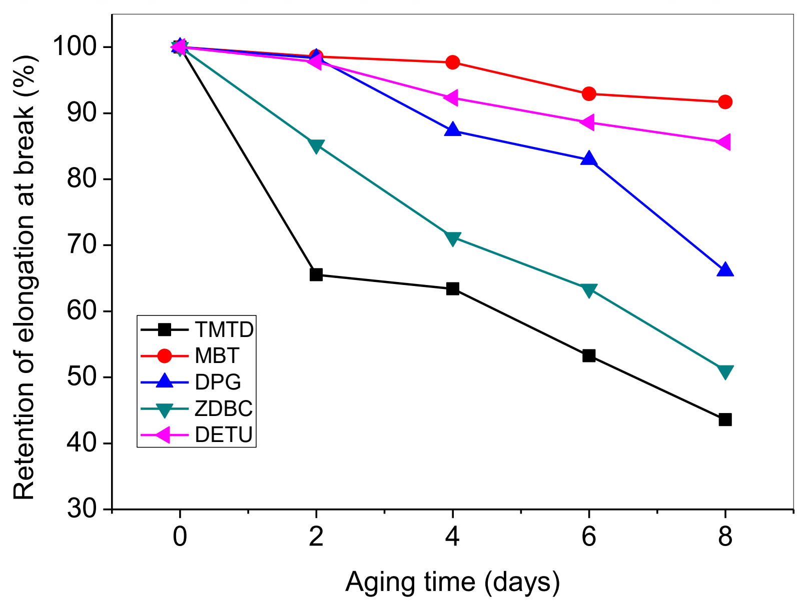

Fig. 4.43. Retention of elongation at break after weathering for SEV system

Table 4.22. Tensile strength, elongation at break and retention values of these properties for EV system

Accelerator	Weathering time (days)	0	2	4	6	8
TMTD	Tensile strength (MPa)	20.78	20.63	20.58	19.71	19.54
TMTD	Elongation at break (%)	820	810	792	743	731
TMTD	Retention of tensile strength (%)	100	99	99	94	94
TMTD	Retention of elongation (%)	100	99	97	91	89
MBT	Tensile strength (MPa)	13.15	12.94	12.72	12.78	12.33
MBT	Elongation at break (%)	790	786	780	783	772
MBT	Retention of tensile strength (%)	100	98	97	97	94
MBT	Retention of elongation (%)	100	99	98	99	97
DPG	Tensile strength (MPa)	12.25	12.10	11.58	10.35	9.86
DPG	Elongation at break (%)	701	692	690	677	647
DPG	Retention of tensile strength (%)	100	97	94	84	80
DPG	Retention of elongation (%)	100	99	98	96	92
ZDBC	Tensile strength (MPa)	13.19	12.53	12.01	11.22	11.17
ZDBC	Elongation at break (%)	927	876	813	783	774
ZDBC	Retention of tensile strength (%)	100	95	91	85	84
ZDBC	Retention of elongation (%)	100	94	87	84	83
DETU	Tensile strength (MPa)	13.49	13.06	12.703	12.654	12.57
DETU	Elongation at break (%)	860	857	849	838	827
DETU	Retention of tensile strength (%)	100	97	95	94	93
DETU	Retention of elongation (%)	100	99	98	97	96

Figures 4.44 and 4.45 show retention values of tensile strength and elongation at break for vulcanizates cured using efficient vulcanization system respectively.

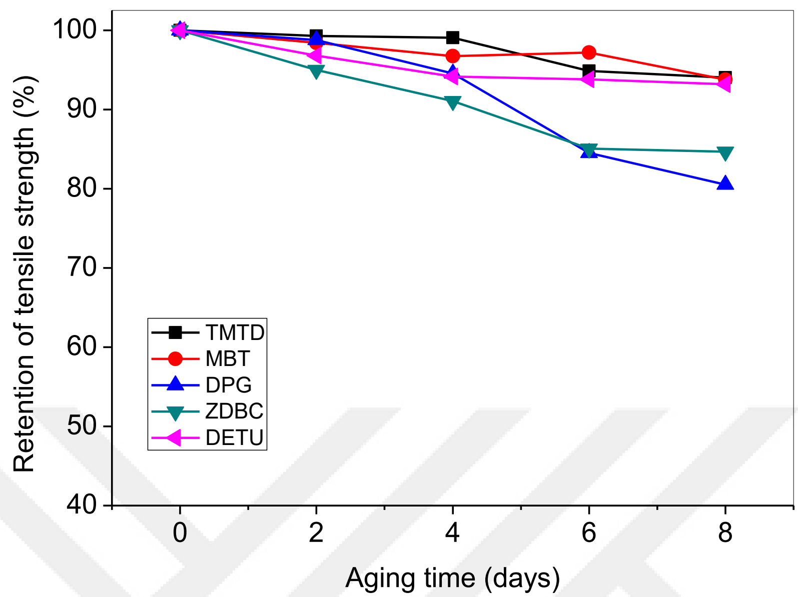

Fig. 4.44. Retention of tensile strength after weathering for EV system

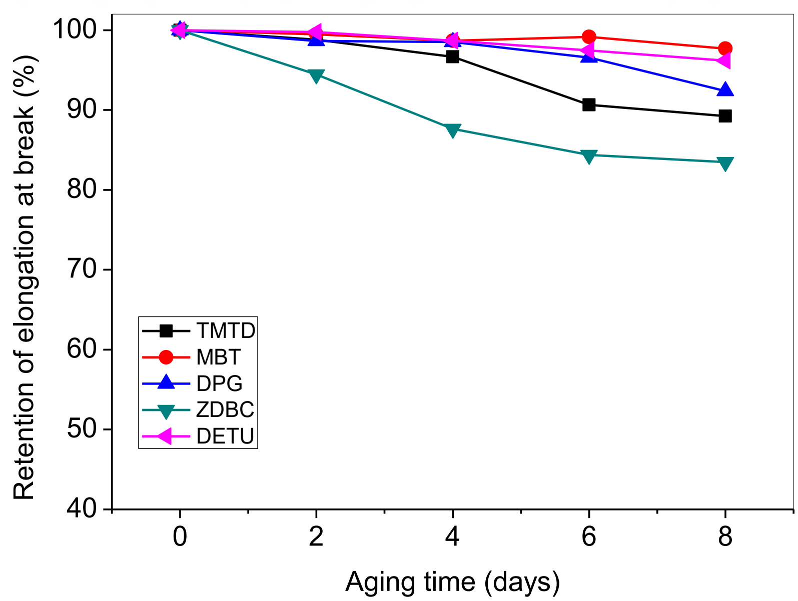

Fig. 4.45. Retention of elongation at break after weathering for EV system

Initial modulus and modulus at 100 and 300% strain values for different accelerators cured using CV, SEV and EV vulcanization systems before and after weathering, have been listed in Tables 4.23-27. These values are in accord with other mechanical properties and are presented to aid comparison between elastic behavior of the vulcanizates.

Table 4.23. Initial modulus and modulus at 100 and 300% strain for TMTD accelerated vulcanizates

	Initial Modulus			Modulus at 100% strain			Modulus at 300% strain		
Weathering Time (days)	CV	SEV	EV	CV	SEV	EV	CV	SEV	EV
0	9.97	11.20	5.49	2.81	3.18	1.42	3.64	3.75	1.89
2	12.40	12.70	6.81	2.78	3.62	1.80	3.67	4.40	2.54
4	12.50	13.10	6.52	3.01	3.71	1.78	3.84	4.43	2.52
6	12.90	13.20	6.16	2.89	4.12	1.80	3.05	4.52	2.64
8	13.10	14.08	6.77	2.99	4.29	1.87	3.10	-	2.66

Table 4.24. Initial modulus and modulus at 100 and 300% strain for MBT accelerated vulcanizates

	Initial Modulus			Modulus at 100% strain			Modulus at 300% strain		
Weathering Time (days)	CV	SEV	EV	CV	SEV	EV	CV	SEV	EV
0	8.59	11.90	7.35	1.60	2.01	1.04	2.15	2.66	1.44
2	8.64	13.30	7.42	1.61	2.74	1.04	2.29	3.30	1.47
4	8.88	14.10	7.54	1.70	2.80	0.98	2.40	3.55	1.55
6	8.95	14.20	8.08	1.72	2.83	1.18	2.38	3.58	1.65
8	10.00	14.40	8.19	1.79	2.92	1.14	2.42	3.76	1.67

Table 4.25. Initial modulus and modulus at 100 and 300% strain for DPG accelerated vulcanizates

	Initial Modulus			Modulus at 100% strain			Modulus at 300% strain		
Weathering Time (days)	CV	SEV	EV	CV	SEV	EV	CV	SEV	EV
0	7.44	10.40	7.84	1.80	2.03	1.30	2.51	2.67	1.57
2	7.60	10.50	8.33	2.00	1.88	1.44	2.86	2.57	1.67
4	8.10	12.20	9.11	2.12	2.27	1.51	2.92	3.01	1.55
6	8.46	13.50	9.36	2.02	2.39	1.50	2.84	3.10	1.68
8	9.02	15.70	14.80	2.03	3.11	1.54	2.84	3.65	1.72

Table 4.26. Initial modulus and modulus at 100 and 300% strain for ZDBC accelerated vulcanizates

	Initial Modulus			Modulus at 100% strain			Modulus at 300% strain		
Weathering Time (days)	CV	SEV	EV	CV	SEV	EV	CV	SEV	EV
0	2.61	2.94	1.71	0.89	1.04	0.85	0.98	1.15	1.05
2	2.73	3.44	2.42	0.89	1.29	0.86	0.96	1.42	1.06
4	3.42	3.84	2.89	1.04	1.50	1.00	1.15	1.53	1.04
6	3.49	4.24	2.50	1.17	1.61	1.02	1.23	1.62	1.21
8	3.59	4.37	2.74	1.11	1.65	1.03	1.25	1.70	1.23

Table 4.27. Initial modulus and modulus at 100 and 300% strain for DETU accelerated vulcanizates

	Initial Modulus			Modulus at 100% strain			Modulus at 300% strain		
Weathering Time (days)	CV	SEV	EV	CV	SEV	EV	CV	SEV	EV
0	2.60	3.53	3.04	0.78	1.29	1.00	0.92	1.40	1.16
2	2.62	3.49	2.98	0.82	1.27	0.98	0.93	1.39	1.17
4	2.78	3.58	2.99	0.86	1.34	1.01	1.08	1.53	1.16
6	2.87	3.67	3.10	0.91	1.41	1.09	1.07	1.54	1.20
8	2.94	3.83	3.00	0.94	1.47	1.04	1.12	1.58	1.21

Accelerated weathering has significantly reduced both tensile strength and elongation properties. This is quite normal considering the poor weathering resistance of natural rubber based elastomeric materials.

Comparison of vulcanization systems indicates that, the vulcanizates cured using semi-efficient vulcanization system exhibit the poorest weathering performance. As for example retention of tensile strength and elongation for the TMTD-accelerated vulcanizate are 56 and 43, respectively. The same data pair is 80 and 82 for conventional and 94 and 89 for efficient vulcanization system in the case of TMTD-accelerated elastomers. The same pattern is followed by the other accelerators. Therefore, when it comes to weathering performance, semi-efficient system is the worst option to choose. It is good to remember that the SEV system has the highest reversion tendency among all of the systems.

When it comes to choose between CV and EV systems, as one can guess the EV system with lower sulfur content exhibits excellent weathering performance due to shorter and more stable sulfur crosslinks.

Comparing the effect of accelerator type, we can see that except for the DETU-accelerated vulcanizate the slower accelerator groups show better weathering performance. MBT accelerator will certainly be the accelerator of choice as far as weathering is the main concern.

Therefore, the general conclusion is that accelerators with moderate cure rates, which provides sulfur with the enough time to rearrange itself and form higher ratios of mono and disulfidic to crosslinks, are preferable compared to faster accelerators when a better weathering performance is required.

However, no need to mention that DETU-accelerator, which is a member of new generation fast accelerators, seems to have the ability to overcome the classical weathering problem of fast accelerators.

Comparing the vulcanization systems, it can be concluded that:

- SEV system has the worst performance.
- ZDBC has very poor performance regardless of vulcanization system.

Comparing the accelerators, it can be concluded that:

- DETU has quite good weathering resistance and it is much better than TMTD.

4.6. Effect of Weathering on Cross-link Density of NR/CR Vulcanizates

Pulse NMR test for the vulcanizates after the weathering have been performed at exactly same conditions to keep comparability. Tables 4.28-4.30 show the results for conventional, semi-efficient and efficient vulcanization systems respectively. Figure 4.46-4.48 represents change in crosslink density because of weathering.

Table 4.28. Pulse-NMR results for differently accelerated vulcanizates cured using CV system

Accelerator Type	Weathering Time (days)	0	2	4	6	8
TMTD	q_0	1.95E-05	1.95E-05	1.95E-05	1.95E-05	1.95E-05
TMTD	q	5.46E-05	7.04E-05	7.10E-05	7.15E-05	7.18E-05
TMTD	M_c (g/mol)	1.27E+04	1.06E+04	1.05E+04	1.05E+04	1.04E+04
TMTD	XLD (mol/cm^3)	1.18E-04	1.42E-04	1.43E-04	1.43E-04	1.44E-04
MBT	q_0	1.60E-05	1.60E-05	1.60E-05	1.60E-05	1.60E-05
MBT	q	2.80E-05	3.18E-05	3.28E-05	3.35E-05	3.82E-05
MBT	M_c (g/mol)	2.18E+04	1.90E+04	1.84E+04	1.81E+04	1.60E+04
MBT	XLD (mol/ cm^3)	6.88E-05	7.90E-05	8.14E-05	8.30E-05	9.37E-05
DPG	q_0	1.55E-05	1.55E-05	1.55E-05	1.55E-05	1.55E-05
DPG	q	3.09E-05	3.49E-05	3.70E-05	4.10E-05	4.40E-05
DPG	M_c (g/mol)	1.92E+04	1.71E+04	1.63E+04	1.49E+04	1.41E+04
DPG	XLD (mol/ cm^3)	7.80E-05	8.75E-05	9.21E-05	1.00E-04	1.06E-04
ZDBC	q_0	1.73E-05	1.73E-05	1.73E-05	1.73E-05	1.73E-05
ZDBC	q	3.05E-05	3.18E-05	3.45E-05	3.44E-05	3.72E-05
ZDBC	M_c (g/mol)	2.08E+04	1.98E+04	1.82E+04	1.83E+04	1.69E+04
ZDBC	XLD (mol/ cm^3)	4.81E-05	5.05E-05	5.49E-05	5.46E-05	5.90E-05
DETU	q_0	1.86E-05	1.86E-05	1.86E-05	1.86E-05	1.86E-05
DETU	q	3.04E-05	3.16E-05	3.28E-05	3.36E-05	3.44E-05
DETU	M_c	2.20E+04	2.09E+04	2.00E+04	1.95E+04	1.90E+04
DETU	XLD (mol/ cm^3)	4.55E-05	4.78E-05	5.00E-05	5.12E-05	5.27E-05

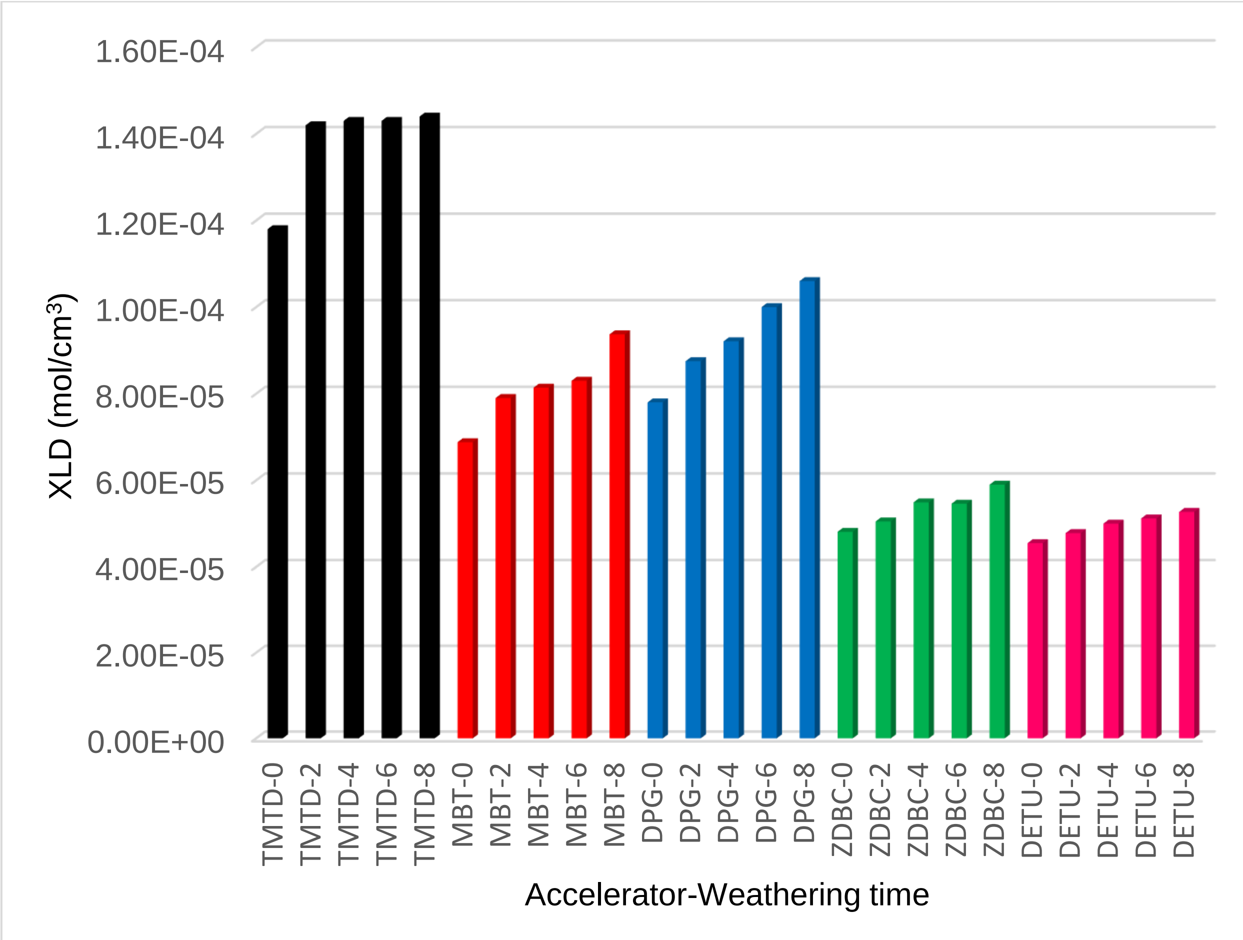

Fig. 4.46. Crosslink density change because of weathering for CV system

From these result we can conclude that as it was expected, for all of the vulcanizates weathering has increased the crosslinking density.

Table 4.29. Pulse-NMR results for differently accelerated vulcanizates cured using SEV system

Accelerator Type	Weathering Time (days)	0	2	4	6	8
TMTD	q_0	1.79E-05	1.79E-05	1.79E-05	1.79E-05	1.79E-05
TMTD	q	8.21E-05	8.48E-05	8.81E-05	9.22E-05	1.01E-04
TMTD	M_c (g/mol)	9.42E+03	9.23E+03	9.01E+03	8.76E+03	8.30E+03
TMTD	XLD (mol/cm^3)	1.59E-04	1.62E-04	1.66E-04	1.71E-04	1.81E-04
MBT	q_0	1.80E-05	1.80E-05	1.80E-05	1.80E-05	1.80E-05
MBT	q	4.54E-05	5.36E-05	5.47E-05	5.51E-05	6.76E-05
MBT	M_c (g/mol)	1.44E+04	1.26E+04	1.25E+04	1.24E+04	1.07E+04
MBT	XLD (mol/ cm^3)	1.04E-04	1.19E-04	1.20E-04	1.21E-04	1.40E-04
DPG	q_0	1.70E-05	1.70E-05	1.70E-05	1.70E-05	1.70E-05
DPG	q	4.13E-05	4.58E-05	4.61E-05	4.66E-05	5.85E-05
DPG	M_c (g/mol)	1.53E+04	1.41E+04	1.40E+04	1.39E+04	1.17E+04
DPG	XLD (mol/ cm^3)	9.78E-05	1.07E-04	1.07E-04	1.08E-04	1.28E-04
ZDBC	q_0	1.75E-05	1.75E-05	1.75E-05	1.75E-05	1.75E-05
ZDBC	q	3.99E-05	5.16E-05	5.33E-05	5.54E-05	6.02E-05
ZDBC	M_c (g/mol)	1.59E+04	1.29E+04	1.26E+04	1.23E+04	1.15E+04
ZDBC	XLD (mol/ cm^3)	9.41E-05	1.16E-04	1.19E-04	1.22E-04	1.30E-04
DETU	q_0	1.67E-05	1.67E-05	1.67E-05	1.67E-05	1.67E-05
DETU	q	5.48E-05	6.00E-05	6.26E-05	6.56E-05	6.37E-05
DETU	M_c	1.22E+04	1.15E+04	1.11E+04	1.08E+04	1.10E+04
DETU	XLD (mol/ cm^3)	1.23E-04	1.31E-04	1.35E-04	1.39E-04	1.36E-04

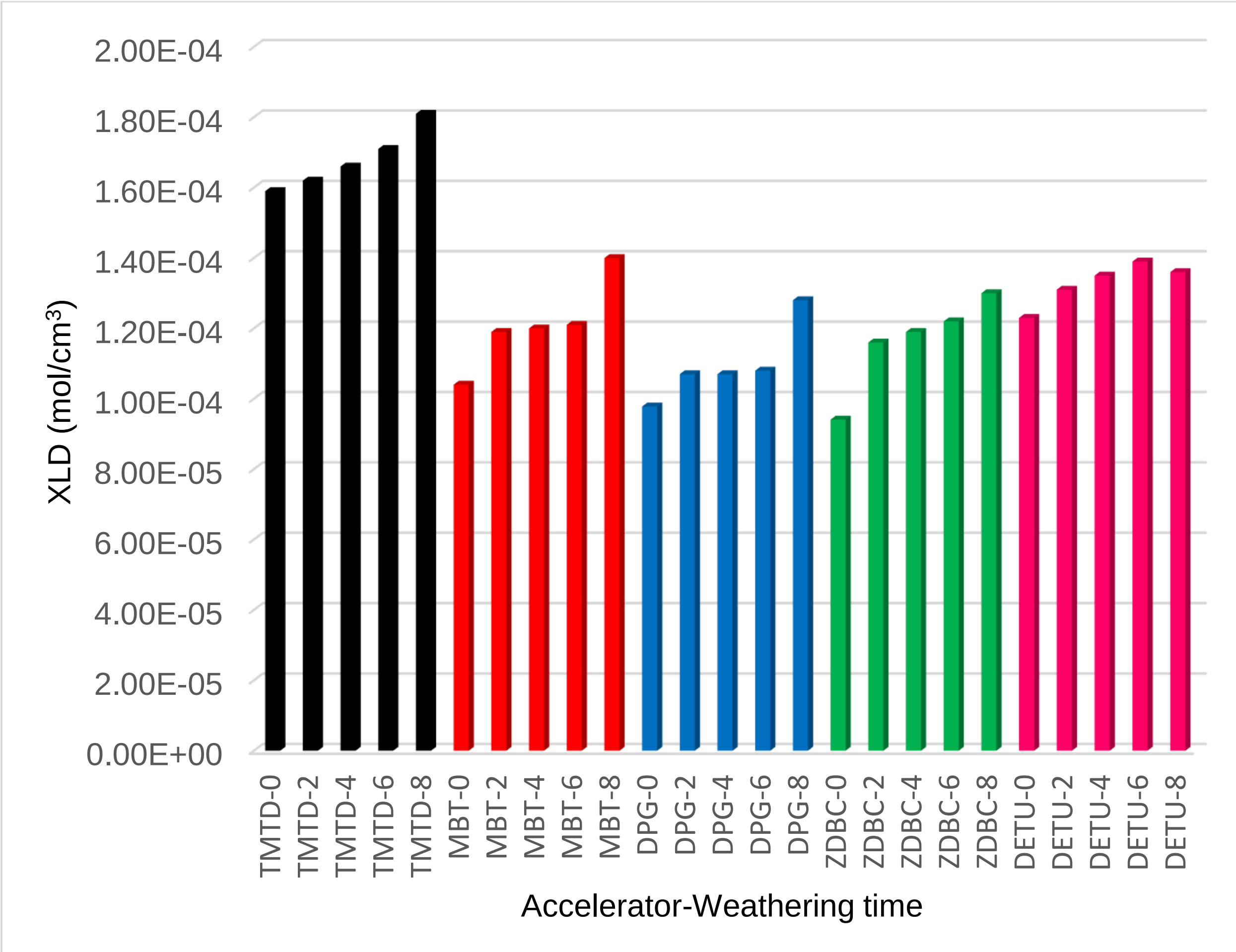

Fig. 4.47. Crosslink density change because of weathering for SEV system

Table 4.30. Pulse-NMR results for differently accelerated vulcanizates cured using EV system

Accelerator Type	Weathering Time (days)	0	2	4	6	8
TMTD	q_0	1.93E-05	1.93E-05	1.93E-05	1.93E-05	1.93E-05
TMTD	q	4.70E-05	5.12E-05	5.29E-05	5.55E-05	5.69E-05
TMTD	M_c (g/mol)	1.44E+04	1.34E+04	1.30E+04	1.26E+04	1.23E+04
TMTD	XLD (mol/cm^3)	1.04E-04	1.12E-04	1.15E-04	1.20E-04	1.22E-04
MBT	q_0	1.82E-05	1.82E-05	1.82E-05	1.82E-05	1.82E-05
MBT	q	2.39E-05	2.47E-05	2.63E-05	2.73E-05	2.83E-05
MBT	M_c (g/mol)	3.18E+04	2.96E+04	2.67E+04	2.51E+04	2.38E+04
MBT	XLD (mol/ cm^3)	4.71E-05	5.06E-05	5.63E-05	5.97E-05	6.31E-05
DPG	q_0	1.77E-05	1.77E-05	1.77E-05	1.77E-05	1.77E-05
DPG	q	2.21E-05	2.25E-05	2.29E-05	2.33E-05	2.36E-05
DPG	M_c (g/mol)	3.61E+04	3.46E+04	3.29E+04	3.17E+04	3.09E+04
DPG	XLD (mol/ cm^3)	4.16E-05	4.34E-05	4.55E-05	4.73E-05	4.85E-05
ZDBC	q_0	1.71E-05	1.71E-05	1.71E-05	1.71E-05	1.71E-05
ZDBC	q	3.14E-05	3.62E-05	3.76E-05	3.85E-05	3.94E-05
ZDBC	M_c (g/mol)	2.00E+04	1.73E+04	1.67E+04	1.63E+04	1.60E+04
ZDBC	XLD (mol/ cm^3)	7.50E-05	8.68E-05	8.99E-05	9.18E-05	9.37E-05
DETU	q_0	1.75E-05	1.75E-05	1.75E-05	1.75E-05	1.75E-05
DETU	q	4.04E-05	4.31E-05	4.61E-05	4.56E-05	4.58E-05
DETU	M_c	1.58E+04	1.49E+04	1.41E+04	1.42E+04	1.42E+04
DETU	XLD (mol/ cm^3)	9.51E-05	1.00E-04	1.06E-04	1.05E-04	1.06E-04

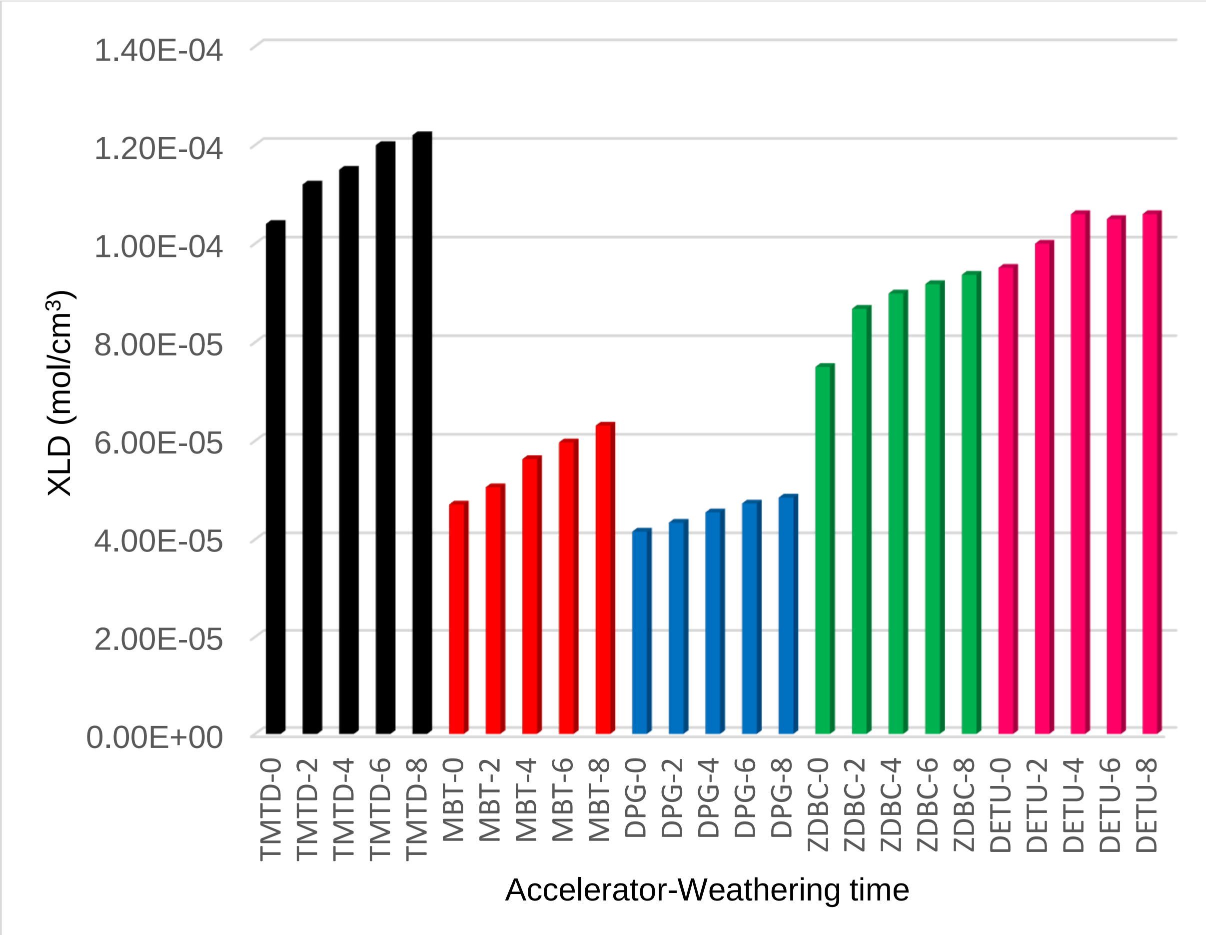

Fig. 4.48. Crosslink density change because of weathering for EV system

Exactly like the XLD results before weathering, the semi-efficient system has the highest XLD for all of the accelerators. Therefore, there must be a co-relation between mechanical performance and crosslinking results. However, detailed cross-checking the results shows that this general relation could not be established without considering type of crosslinking. For example, TMTD-accelerated vulcanizate should have a higher rate of XLD increase in CV system, since combination of higher sulfur and faster cure rate must result in the worst weathering performance. However, the important factor here is the higher ratio of poly-sulfidic crosslinks present in this combination. Therefore, weathering seems to start with changing the crosslinks type from unstable poly-sulfidic to more stable mono and di-sulfidic links. During this period, the overall XLD seems to stay more and less the same while, the ratio of XLD type changes in favor of mono and disulfidic links.

The change crosslink type is the main cause of complex stress relaxation patterns obtained from TSSR experiments, which will be discussed in section 4.7.

Comparing the vulcanization systems, it can be concluded that:

- Counting ZDBC out, CV system with the highest sulfur content has the worst performance.

Comparing the accelerators, it can be concluded that:

- Fast group accelerators except ZDBC show good weathering performance.
- DETU has quite good aging performance.
- Like the case of mechanical performance ZDBC has poor weathering resistance especially in case of SEV system.

4.7. Effect of Weathering on Stress Relaxation Behavior of NR/CR Vulcanizates

Stress relaxation tests have been carried out for vulcanizates after weathering. The samples have been stored at room temperature for 48h before the start of relaxation test. Since the differences between the TSSR values are very small for the vulcanizates after 2, 4 and 8 days of weathering, the presented results will show the data for 8 days of weathering cycle. Stress relaxation curves for different accelerator containing vulcanizates cured using different vulcanization systems have been presented in figures 4.49-4.53.

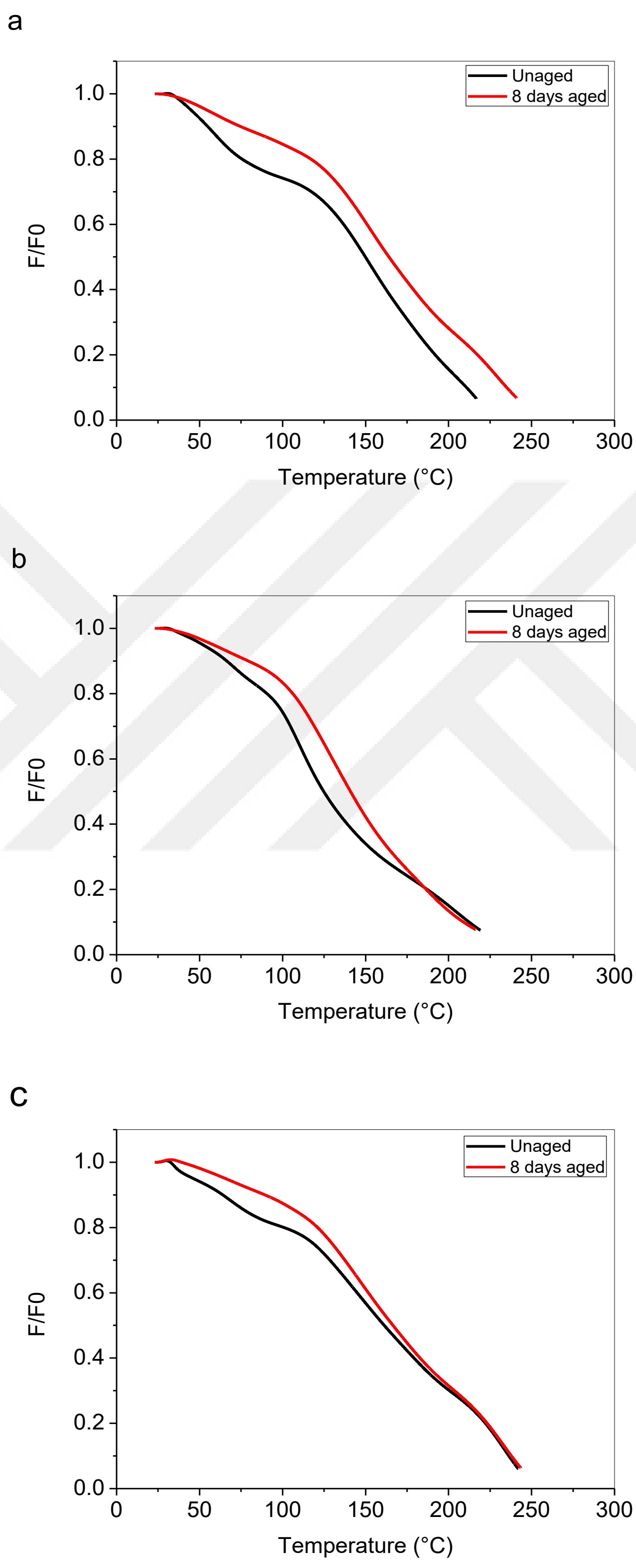

Fig. 4.49. Stress relaxation curve for TMTD-accelerated vulcanizate cured using CV (a), SEV (b) and EV (c) systems, before and after accelerated weathering

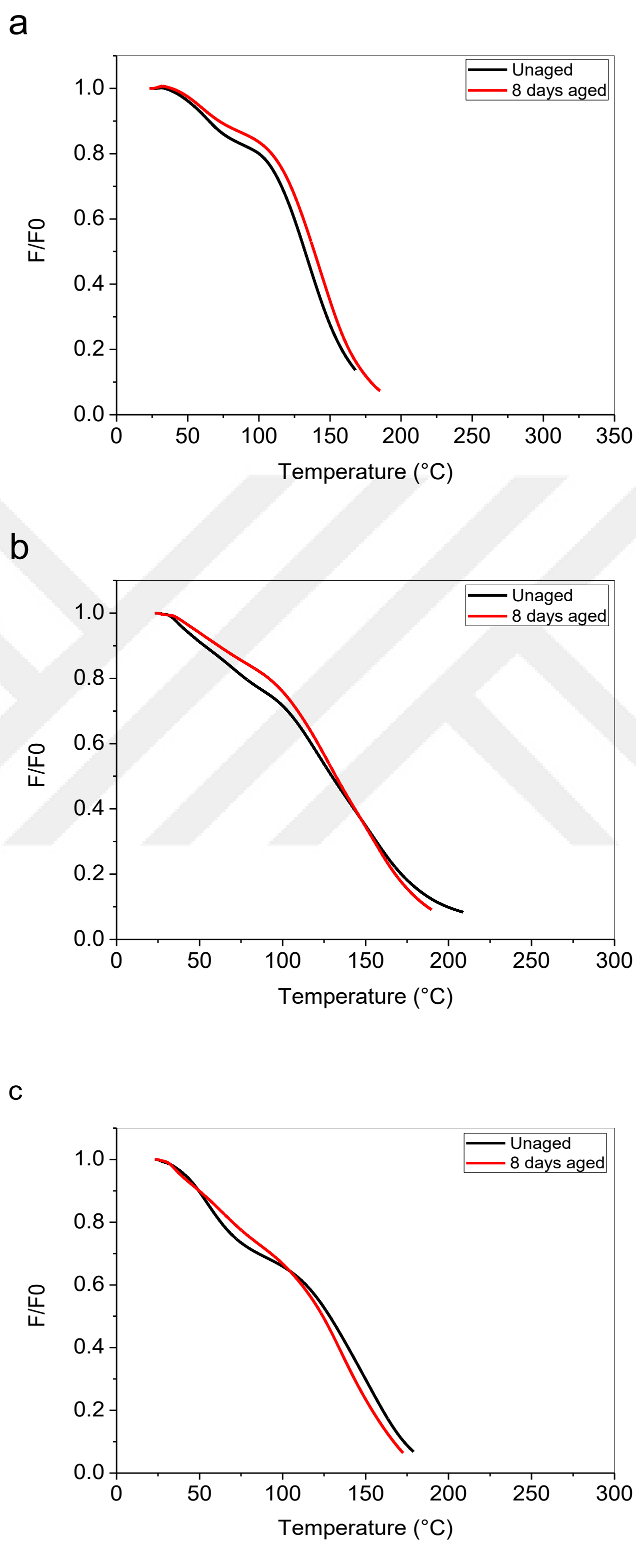

Fig. 4.50. Stress relaxation curve for MBT-accelerated vulcanizate cured using CV (a), SEV (b) and EV (c) systems, before and after accelerated weathering

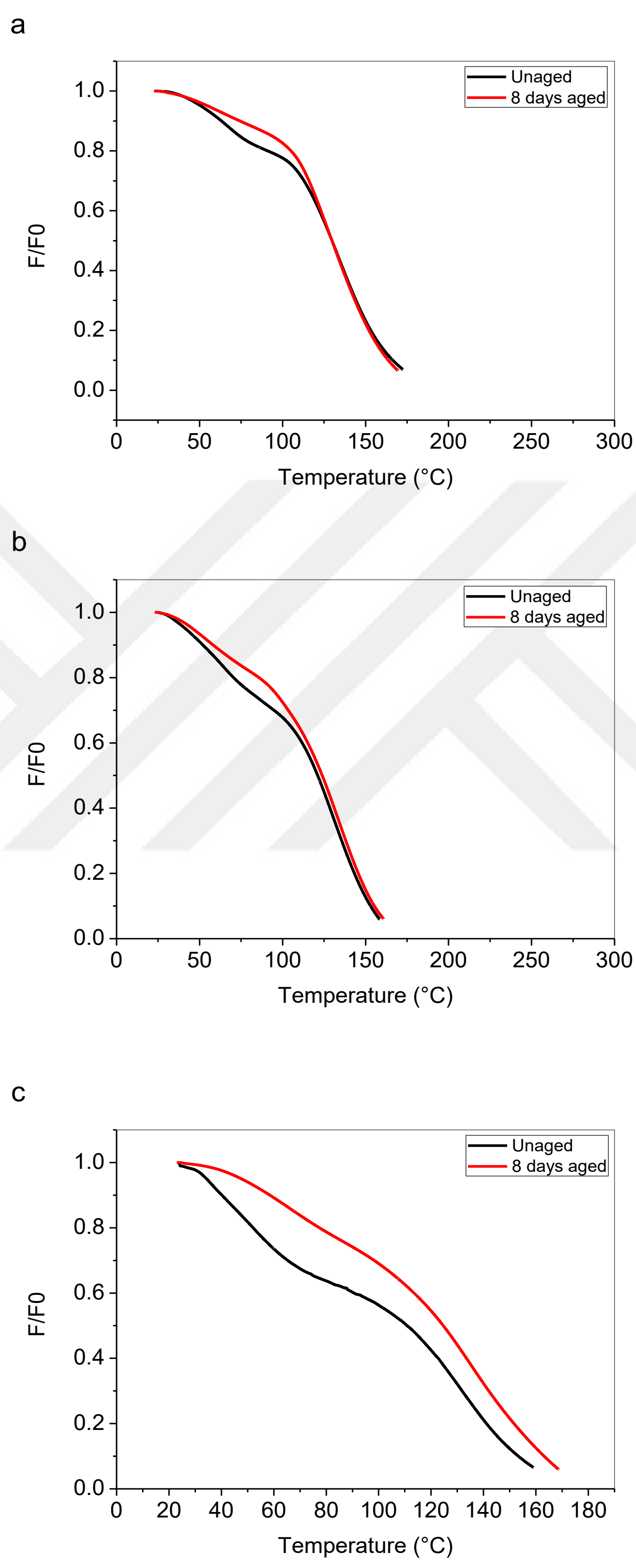

Fig. 4.51. Stress relaxation curve for DPG-accelerated vulcanizate cured using CV (a), SEV (b) and EV (c) systems, before and after accelerated weathering

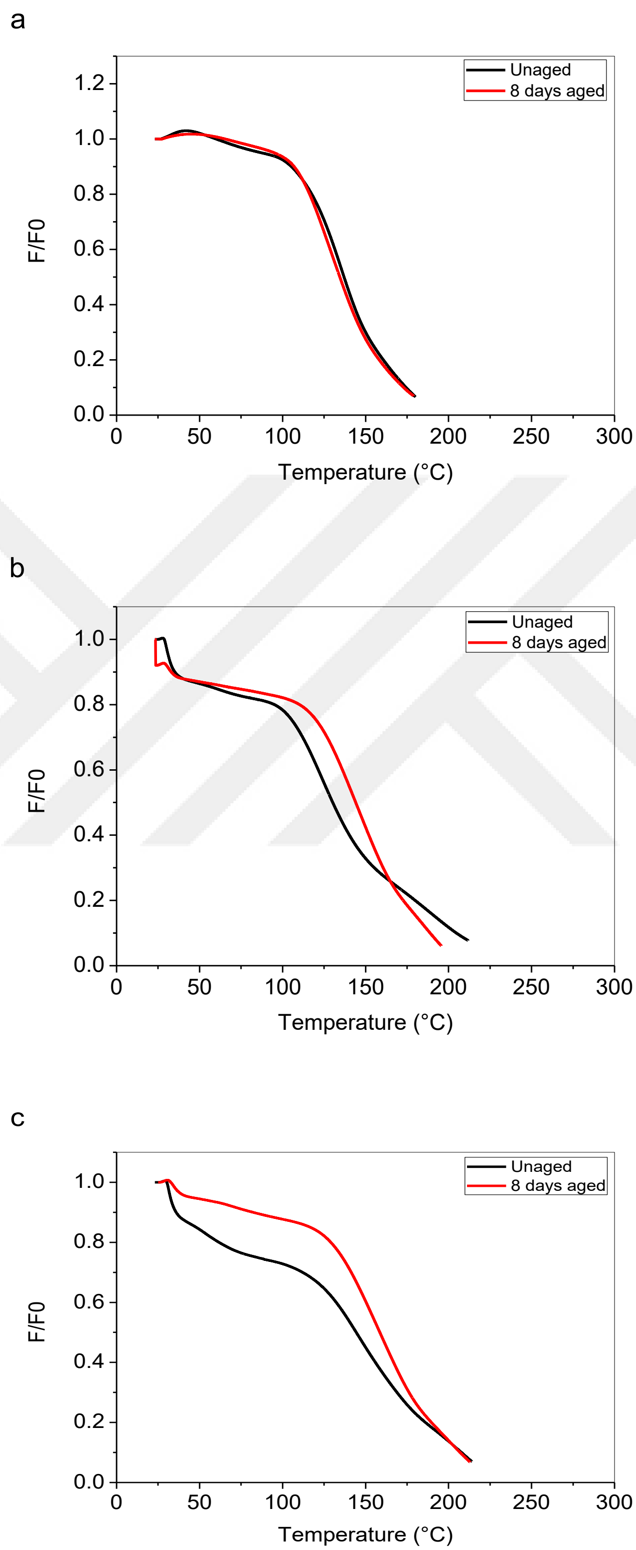

Fig. 4.52. Stress relaxation curve for ZDBC-accelerated vulcanizate cured using CV (a), SEV (b) and EV (c) systems, before and after accelerated weathering

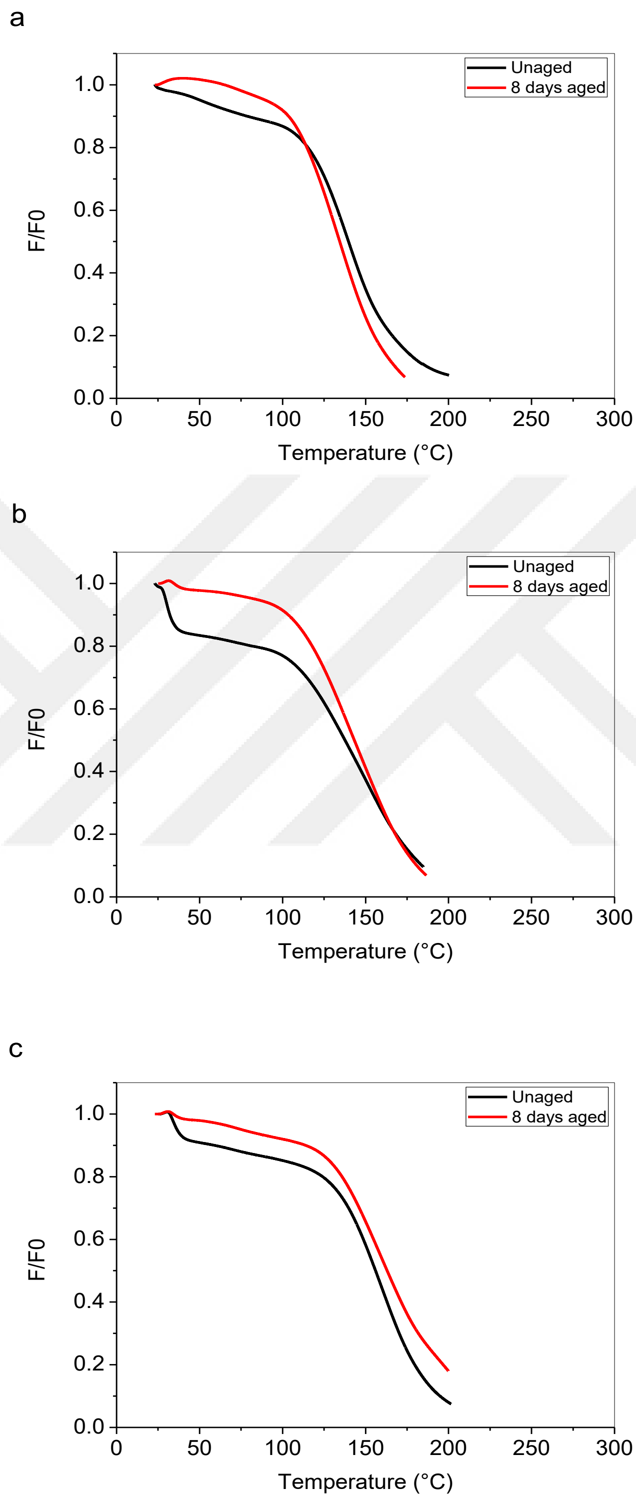

Fig. 4.53. Stress relaxation curve for DETU-accelerated vulcanizate cured using CV (a), SEV (b) and EV (c) systems, before and after accelerated weathering

Tables 4.31-4.33 summarize TSSR analysis results.

Table 4.31. TSSR data for vulcanizates cure using CV system

Accelerator type-Weathering time	σ_0 (MPa)	T_{10} (°C)	T_{50} (°C)	T_{90} (°C)	TSSR Index
TMTD-0	0.99	54.9	149.9	210.8	0.63
TMTD-8	1.33	64.6	153.1	225.0	0.65
MBT-0	0.67	72.0	139.0	178.8	0.71
MBT-8	0.93	65.1	132.5	167.9	0.71
DPG-0	0.85	63.2	129.8	166.5	0.69
DPG-8	0.97	68.3	129.8	163.7	0.72
ZDBC-0	0.53	78.6	139.8	187.5	0.70
ZDBC-8	0.54	100.0	134.5	173.0	0.76
DETU-0	0.52	105.3	137.1	174.4	0.76
DETU-8	0.57	103.6	134.5	168.1	0.77

Table 4.32. TSSR data for vulcanizates cure using SEV system

Accelerator type-Weathering time	σ_0 (MPa)	T_{10} (°C)	T_{50} (°C)	T_{90} (°C)	TSSR Index
TMTD-0	1.27	66.4	124.8	212.3	0.60
TMTD-8	1.75	79.4	141.0	209.0	0.64
MBT-0	1.14	53.0	129.8	199.2	0.59
MBT-8	1.30	61.4	132.1	187.2	0.64
DPG-0	0.84	52.0	121.2	153.0	0.67
DPG-8	1.02	58.1	123.9	150.3	0.70
ZDBC-0	0.85	32.1	137.6	184.0	0.65
ZDBC-8	1.01	54.0	142.7	181.2	0.69
DETU-0	0.79	35.1	130.3	204.7	0.60
DETU-8	0.95	103.4	143.2	180.9	0.74

Table 4.33. TSSR data for vulcanizates cure using EV system

Accelerator type-Weathering time	σ_0 (MPa)	T_{10} (°C)	T_{50} (°C)	T_{90} (°C)	TSSR Index
TMTD-0	0.82	64.0	161.3	236.4	0.60
TMTD-8	0.95	89.4	166.5	237.8	0.64
MBT-0	0.39	49.5	128.4	173.1	0.63
MBT-8	0.65	49.8	124.3	167.0	0.64
DPG-0	0.50	40.2	110.9	153.3	0.59
DPG-8	0.56	58.5	124.7	150.2	0.67
ZDBC-0	0.61	113.9	163.0	212.9	0.69
ZDBC-8	0.70	82.3	158.6	207.0	0.70
DETU-0	0.52	35.9	144.4	207.8	0.59
DETU-8	0.71	59.0	156.0	194.9	0.71

Looking at stress relaxation cures before and after weathering, one can easily conclude that for all of the vulcanizate, weathering have improved overall relaxation behavior (Stress decrease has been shifted to higher temperatures).

Comparing the initial stress (σ_0) values shows that this value increases because of weathering for all of the vulcanizates and as discussed before (section 4.4) it can be related to the XLD of the vulcanizates.

The same pattern of CV>SEV>EV for TSSR index for vulcanizates before weathering exists here and weathering seems to improved TSSR index when comparison made for both accelerator and vulcanization system cases.

Except for TMTD-accelerated vulcanizate maximum service temperature (T_{90}) reduced as a result of weathering. This can be related to loss of flexibility caused by weathering. More rigid polymer chains and crosslinks could not resist heat buildup as good as their more flexible condition prior to weathering.

Weathering also seems to reduce the slope of stress decrease especially for the temperatures up to 100°C (the temperatures under the maximum heat resistance temperatures for both NR and CR rubbers). For example, in the case of DPG-accelerated CV cured vulcanizate, normalize stress value at 100°C is around 0.8 for unaged and 0.9 for aged sample. Since longer polysulfidic crosslinks facilitate stress reduction, we can conclude that weathering reduces the polysulfidic crosslink ratio. Another evidence for this phenomenon can be observed by comparing the accelerator type effect, where the difference between the stress relaxation patterns before and after weathering is bigger for fast group accelerators.

Detailed studies of these stress relaxation curves will reveal complexities that are hard to describe without more evidence. Considering the fact that change in crosslinking type and density, main chain scission process, formation of unbounded sulfur which can all happen as a result of weathering, combined by reversion phenomena that is dominant factor for NR based elastomers above 150°C can dramatically change relaxation behavior, makes it difficult if not impossible to find specific patterns for stress relaxation of NR based vulcanizates.

Comparing the vulcanization systems, it can be concluded that:

- CV system has the best relaxation performance and highest service temperature

Comparing the accelerators, it can be concluded that:

- Fast group accelerators show better relaxation performances after weathering.

  .

5. CONCLUSIONS

In the scope of this thesis, it has been tried to reveal the effect of accelerator type and accelerator to sulfur ratio (vulcanization system) on mechanical and thermomechanical properties of the NR/CR vulcanizates and their network structure. The main conclusions are listed below;

- Both accelerator type and vulcanization system have dominant effect on thermal and thermomechanical properties of the NR/CR vulcanizates. Since these factors, change crosslink type and density, they also dominate the network structure of the vulcanizates. Weathering performance is closely related to the crosslinking type and density so it also changes with the change of both accelerator type and vulcanization systems.
- Considering the reversion phenomena, which is dominant at temperatures above 150°C for NR/CR compounds, semi efficient system has the highest reversion rate. Therefore, either reduction of cure temperature or revising of vulcanization system should be considered especially if the cure system applied to cure large-sized vulcanizates.
- Considering the cure rate we can conclude that, as it was expected from their group names, the pattern is TMTD>MBT>DPG. However, ZDBC and DETU despite the group that they belong have rather small cure rate values. This fact combined with their low cure extent and especially low maximum torque value places them far from being an alternative for TMTD accelerator at least in the case of NR based rubber vulcanizates. This conclusion is also supported with mechanical tests and crosslinking density test results.
- Semi-efficient system shows the overall best mechanical performance and has the highest crosslink density when the systems are compared. TMTD accelerated vulcanizates show the best performance in these aspects.
- There is a good inter dependency between the cure extent values obtained from MDR rheometer and crosslink densities obtained from pulse NMR.
- Conventional vulcanization system exhibit superior relaxation performance which drops down around the 140°C due to the lower reversion resistance. This

reversion related relaxation drop is more obvious in fast accelerator groups (TMTD, ZDBC and DETU) where the higher cure rates probably leads to more polysulfidic crosslinks, which in turn could cause enhanced reversion behavior. Comparing the initial stress (σ_0) values and XLD values show the more crosslinked vulcanizates exhibit higher initial stress values.

- Accelerated weathering (weathering) significantly reduced both tensile strength and elongation properties. The higher free sulfur amount present at CV system accelerates weathering process. Therefore, from the weathering aspect we can conclude that the fewer sulfur amount equals the better weathering performance. Comparing the accelerator type show that except for the DETU-accelerated vulcanizates, the slower accelerator groups show better weathering performance.
- DETU-accelerator, which is a member of new generation of fast accelerators, seems to have the ability to overcome the classical weathering problem of fast accelerators however, has it has rather low cure efficiency.
- XLD increases as a result of weathering; however, it is not possible to relate XLD change to weathering without considering the crosslink type (mono, di or polysulfidic).
- The combination of crosslink type and crosslink density cause complex stress relaxation patterns, which are hard to describe in detail but TSSR technique provides important data related to the network structure of vulcanizates. These data combined with pulse NMR data can be used to reveal the structural differences caused because of weathering.
- In the cases that maximum dynamic and relaxation has higher priority, CV system should be the system of choice.
- In the caces that maximum weathering performance has the priority, EV system should be the system of choice.
- In the cases that maximum mechanical performance has the priority, SEV system should be the system of choice.

- TMTD accelerator combines highest mechanical performance with good relaxation and weatherability. DETU also is a good choice in these regards and do not have any health issues.
- MBT and DETU both have the potential to replace TMTD, but DETU seems to have all the advantages of fast group accelerators except for cure efficiency that must be developed with more detailed research.
- DPG and ZDBC are not a good accelerator choice for NR/CR compounds, regardless of vulcanization systems.

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2. F. Ahmadzadeh Nobari Azar, A. Babapour, M. Şen. "Variation of Mechanical Properties and Thermal Aging Behaviors of Natural Rubber/Chloroprene Rubber Blends As A Result of Change In Accelerator Type", *International Seminar on Elastomers (ISE)* Bratislava, Slovakia , 24-28 August 2014
3. F. Ahmadzadeh Nobari Azar, A. Babapour, M. Şen, B.Karaağaç, V.Deniz. *"Determination of the Effects of Accelerator Type and Accelerator/Sulfur Ratio on the Vulcanization Kinetics of Natural Rubber/Chloroprene Rubber Compounds"*, RubberCon 2013,Bangkok, Thailand,16-18 December 2013

Publication as a Book Section

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