

# Insights into Mechanical, Thermal, and Electrical Properties of Peroxide-Cured Chlorinated Polyethylene/Ethylene Methacrylate Copolymer Blend Vulcanizates

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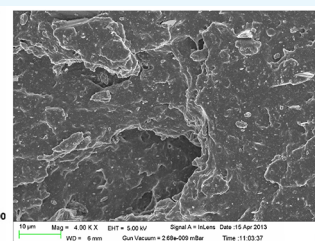
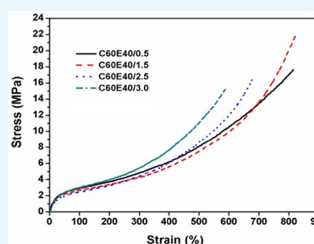


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**ABSTRACT:** This work unveils the effect of chemical modification of compatible elastomer blends based on the chlorinated polyethylene (CPE) and ethylene methacrylate copolymer (EMA) (60:40 ratio) using dicumyl peroxide (DCP). CPE/EMA blend vulcanizates were prepared by varying the DCP concentration from 0.5 to 3.0 wt %. All blend vulcanizates showed significant enhancement in physicochemical properties and thermal stability upon increasing the DCP concentration. DCP incorporation also enhanced the compatibility between CPE and EMA rubbers, which was revealed from FTIR data and other technical properties. Specifically, the vulcanizates with 1.5 wt % DCP showed an enormous improvement in mechanical properties and glass transition temperature ( $T_g$ ) due to various reasons such as cure characteristics, cross-linking densities, co-cross-linking systems, and morphological features. Uniform distribution of DCP in both the elastomeric phases across their interphases caused co-cross-linking, which increased interphase adhesion in the blend vulcanizates. High interphase adhesion of the blend vulcanizates of 1.5 wt % DCP was directly reflected in its improved mechanical, thermal, flame retardation properties and enhanced oil resistance and volume resistivity in comparison to pristine CPE/EMA blend vulcanizates. Also, the volume resistivity and oil resistance properties of blend vulcanizates were found to be marginally improved upon increasing the concentration of DCP.



## 1. INTRODUCTION

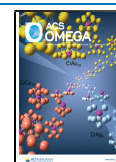
Among polymeric material applications, rubber industries are covering almost half of the market at present. Starting from the commonly known tyre industries and hose and cable industries, rubber is covering a huge area of applications including the automotive sector.<sup>1,2</sup> Today, rubber industries are urging the usage of rubber blends in versatile applications due to the obvious advantage of the combination of unique properties and reduced cost of products.<sup>3,4</sup> The literature suggests that ample research works have been carried out on the successful blending of two or more elastomers with improved synergistic properties.<sup>5–7</sup> It is a fact that elastomers have to be cross-linked/cured to achieve the desired set properties of final products.<sup>8</sup> In the case of saturated polymers/rubbers, peroxide cross-linking and radiation cross-linking also works miraculously.<sup>9</sup> In both cases, the formation of a strong C–C bond between polymer backbone chains provides an additional advantage over conventional sulfur curing of unsaturated polymers. In the case of blends of two or more polymers or elastomers with saturated backbones, peroxide cross-linking has evolved as the most adopted technique in industries.<sup>10</sup> The ability of peroxides to co-cross-link two elastomeric phases at their backbone thrusts a high interphase adhesion between the two phases. Polymer blends with saturated backbones not only undergo effective cross-linking

in the individual phases but also cross-link at the interfacial regions. Hence, peroxides are successfully used in many polymer blends to improve interfacial adhesion and preferred over other curing agents.<sup>11–13</sup> Until now, the major obstructions in developing utilitarian rubber blends using peroxide cross-linking are mainly their mixing homogeneity and cure rate incompatibility.<sup>14</sup> The aforementioned problems can be resolved by chemically modifying either of the polymers or by adding a suitable compatibilizer between the two phases. However, it is difficult to get rid of the problem with cure rate incompatibility. Therefore, judicious selection of elastomers with required criteria for the particular applications and molecular structures close to each other is highly recommended to enhance the compatibility between them. Miscible elastomer blends contain only a single phase where cross-linking takes place uniformly. However, interfacial adhesion of technologically compatible blends exhibiting more than one phase can be improved by the co-cross-linking approach. In such cases,

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curing agents are chosen so that they can cure both the phases simultaneously and also across the interphases. Here, three important factors play a vital role in obtaining technically suitable elastomer blend vulcanizates: the melt viscosity mismatch factor, polarity of two elastomeric phases, and cure rate mismatch factor. The closer the values of these three factors, the higher the extent of co-cross-linking of the two elastomeric phases with a higher degree of cross-linking at the interphases. Maity and Das used DCP as an effective chemical compatibilizer between CPE and polyurethane (PU) with improved interphase adhesion by co-cross-linking.<sup>15</sup> Chlorinated polyethylene (CPE) and ethylene methacrylate copolymer (EMA) elastomers are majorly utilized in flexible cable industries, hoses for transporting fluids, and pipes, and they also have found applications in geomembrane industries. Besides electrical insulating applications, CPE is highly stable and resistant toward ozone, chemicals and solvents, and fires; therefore, it is widely used as a sheathing material. Since both polymers bear large ethylene chains and the polarities of CPE and EMA are close enough, they have great tendency to interact at the molecular level. Moreover, the chlorine group of CPE and the ester group of EMA have some specific interaction, which increases the interfacial adhesion between the two.<sup>16</sup> Dicumyl peroxide (DCP) is the commonly used cross-linking system for CPE and EMA due to its saturated backbone structure.<sup>17–19</sup> In our previous article on the compatibility study of CPE/EMA blends, the 60:40 blend was found to have the finest properties including mechanical strength and thermal stability. However, we have not carried out an investigation of cured CPE/EMA blends to date. To the best of our knowledge, there is no report on vulcanization of the aforesaid blend and its curing mechanisms either the co-cross-linking manner or else. Nevertheless, curing of rubber or rubber blends is very important for the product to maintain the shape fidelity and durability. Henceforth, based on our previous study, the 60:40 blend of CPE/EMA is used in the present study to investigate the effect of DCP as a co-cross-linking agent for improving compatibility between the two elastomeric phases. Consistent and optimum cross-linking across the interfaces in polymer blend systems has a profound effect on improving mechanical and other technical properties. By considering all of these factors, the effect of DCP concentration on physical characteristics, mechanical properties, and thermal stability of the blends of CPE/EMA having a 60:40 ratio is evaluated and discussed thoroughly in the current work.

## 2. RESULTS AND DISCUSSION

**2.1. Mechanical Properties.** Effects of the DCP cross-linking system with a varying concentration on the physicochemical properties of C60E40 blends and their vulcanizates are evaluated under tension mode. The stress–strain diagram of all of the cross-linked blend systems is shown in Figure 1. Table 1 displays the obtained physicochemical properties including the strength, modulus, and percentage elongation of C60E40 blends and their vulcanizates.

From Table 1, an approximately 40% improvement in the tensile strength upon addition of a minor amount (0.5 wt %) of DCP was observed. Interestingly, there is a remarkable increment of about 78% in tensile strength upon 1.5 wt % loading of DCP. However, incorporation of more than 1.5 wt % DCP decreased the mechanical property of the vulcanizates. There is an obvious decrease in %elongation at break values on

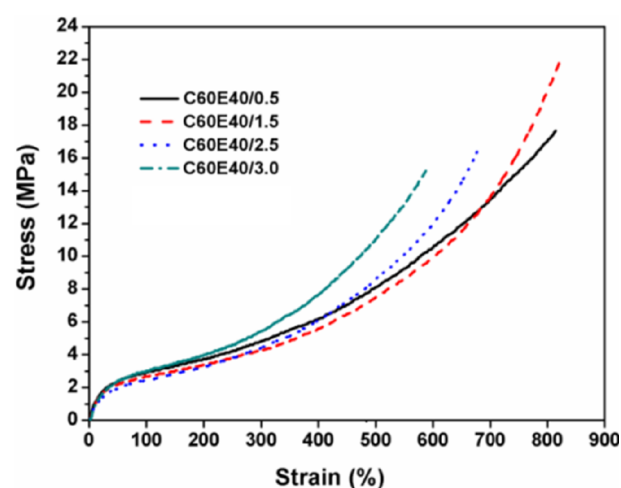


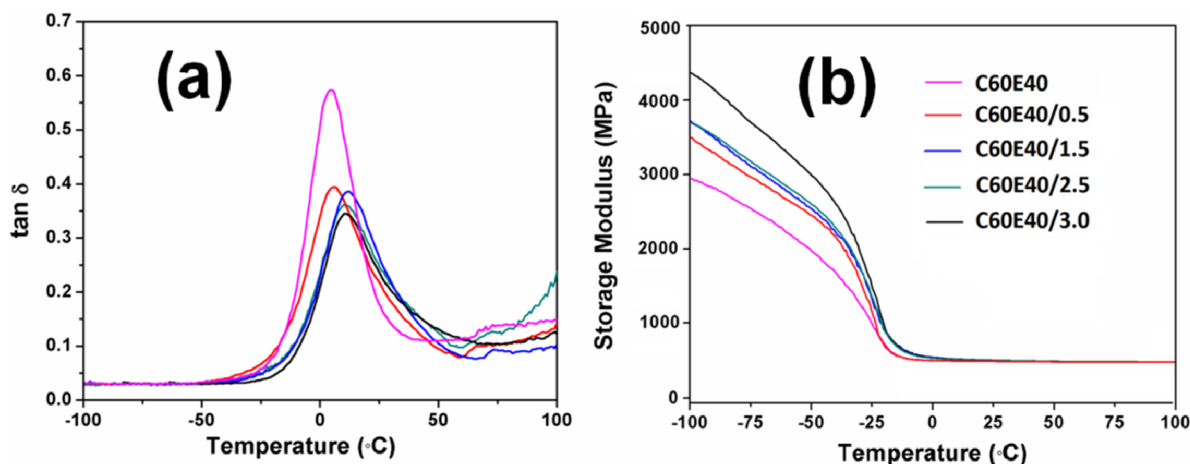
Figure 1. Stress–strain plot of various CPE/EMA blend vulcanizates.

curing, and DCP with 1.5 wt % loadings showed the highest elongation at break with maximum tensile strength among all vulcanizates. This indicates a uniform and optimum cross-linking of the blend with minimal free radical degradation due to peroxides at 1.5 phr DCP loading. Moreover, the modulus at 100% elongation and Shore A hardness kept on increasing with increasing DCP loading due to overcuring. Mechanical properties of elastomer blends depend not only on the extent of cross-linking of individual phases but also on effective cross-linking across the interfaces. In a binary blend, the concept of the optimum peroxide concentration is most likely related to the interface adhesion between the two elastomeric phases. The radical-induced co-cross-linking by peroxides (graft linking) between the two phases further improves the technological compatibility. This interface adhesion between the two elastomeric phases was dependent on the number of interface graft links. The number of interface graft links in turn relies on peroxide until a certain concentration. Beyond this optimum peroxide concentration, the cross-linking density (CLD) starts increasing substantially in the elastomeric phase with a high cure rate index (CRI) due to migration of cross-linking agents.<sup>20</sup> Such migration of cross-linking agents leads to an uneven CLD and poor interfacial cross-linking across the interfaces, which have a direct adverse effect on ultimate tensile properties.

The enhancement in tensile properties of CPE/EMA blend vulcanizates in our study on curing with 1.5 wt % DCP is not only because of a high degree of cross-linking in both the constituent elastomeric phases but also because of consistent cross-linking at the CPE/EMA interphases. This mechanism is known as co-cross-linking, where both elastomeric phases are cross-linked simultaneously with the same cross-linking agent. Cross-linking of both the elastomeric phases across their interphase formed a semi-interpenetrating networklike structure between CPE and EMA. The appearance of this optimum DCP concentration was possibly due to increased adhesion between the two phases.<sup>20</sup> The significant increment in the tensile strength value is likely due to balanced and uniform cross-linking in both the elastomeric phases. Also, massive co-cross-linking around the rubber interphase can cause effective stress transfer under a tensile load, which can be reflected in the improved ultimate tensile strength (UTS) values of the cured blends. To have an in-depth understanding of the tensile behavior of the cross-linked blend systems, a thorough

**Table 1. Tensile Properties of Various CPE/EMA Blend Vulcanizates**

sample codes	tensile strength (MPa)	elongation at break (%)	modulus @ 100% elongation	hardness (shore A)
C60E40/0.0	12.6 ± 0.2	1175 ± 5	1.6 ± 0.2	67 ± 2
C60E40/0.5	17.6 ± 0.1	815 ± 10	2.9 ± 0.1	70 ± 3
C60E40/1.5	22.4 ± 0.3	848 ± 8	2.5 ± 0.2	76 ± 1
C60E40/2.5	16.4 ± 0.1	678 ± 10	2.4 ± 0.1	79 ± 1
C60E40/3.0	15.2 ± 0.2	588 ± 11	3.0 ± 0.2	84 ± 2

**Figure 2.** (a)  $\tan \delta$  and (b) storage modulus ( $E'$ ) vs temperature of un-cross-linked and cross-linked blends of various CPE/EMA blend vulcanizates.

systematic study of the vulcanizates was carried out in the following sections.

**2.2. Dynamic Mechanical Analysis (DMA).** The dynamic micromechanical properties of CPE/EMA (60:40) blends and their vulcanizates were evaluated under temperature sweep mode. Storage modulus ( $E'$ ) and dynamic loss ( $\tan \delta$ ) were measured over the temperature range between  $-100$  and  $100$  °C. The  $\tan \delta$  peak value was calculated from the peak positions, which belong to the segmental motion of the blends ( $T_g$ ). Figure 2a,b displays  $\tan \delta$  and storage modulus ( $E'$ ) against the temperature of un-cross-linked and cross-linked blend vulcanizates. An abrupt decrease in the damping factor (height of the  $\tan \delta$  peak) of vulcanizates compared to that of the neat CPE/EMA (60:40) blend, as can be observed in Figure 2a, is because of the effective degree of cross-linking in the blend system. Similarly, the damping factor showed a decreasing trend upon increasing DCP concentration. Moreover, like a neat CPE/EMA (60:40) blend system, the cross-linked blends exhibited a clear single peak in the  $\tan \delta$  vs temperature plot (Figure 2a). As previously reported by our group, the C60E40 blend shows better compatibility between CPE and EMA.<sup>16</sup> Furthermore, the existence of a single glass transition temperature is clear evidence of the compatibility between CPE and EMA even after cross-linking.<sup>21</sup> This is an indication of uniformity in the cross-linking network around the phases and across their interphases. Furthermore, as the DCP concentration increased, the  $T_g$  value of the corresponding vulcanizates shifted to a higher temperature. This is naturally because of a higher CLD due to the presence of a higher concentration of the cross-linking agent.<sup>22</sup> This increase in  $T_g$  is associated with broadening of the transition peak, as also reported by Bruining et al.<sup>23</sup> The reason could be that the cross-linking networks in the amorphous region restrict the molecular mobility of polymer chains. It is essential to remark that the C60E40 blend exhibits only an amorphous region, as

almost no crystallinity was observed in this blend system in our previous study.<sup>16</sup> Also, the  $\tan \delta$  peak shifting toward a higher temperature along with peak broadening refers to improved compatibility between the two phases.<sup>24</sup> The same observations were reported by many researchers on the effect of CLD on  $T_g$  of blend vulcanizates.<sup>25–27</sup> DMA was also used for reinforcing the co-cross-linking concepts by analyzing the DCP-cured pristine CPE and EMA polymer. Figures S1 and S2 show the storage modulus and  $\tan \delta$  of the 1.5% DCP-cured pristine CPE and EMA polymer, respectively. Figures S1 and S2 reveal the significant improvement of storage modulus and shifting of the  $T_g$  value to a slightly higher degree compared to those of the uncured CPE and EMA polymer.<sup>16</sup> This indicates that CPE and EMA were effectively cured by DCP and it causes co-cross-linking while using it for preparing CPE/EMA blend vulcanizates. All of the characteristic data extracted from the DMA testing is tabulated in Table 2.

In this case, vulcanizate C60E40 with 1.5 wt % DCP concentration showed the highest  $T_g$ . Further, an increase in DCP concentration caused no significant effect on their  $T_g$  values, as can be seen from Table 2. It is speculated that the excess quantity of DCP in C60E40/2.5 and C60E40/3.0 may cause uneven distribution of the CLD. CPE has a higher CRI

**Table 2. Characteristic Data Acquired from DMA of Various CPE/EMA Blend Vulcanizates**

sample designation	glass transition temperature ( $T_g$ ) (°C)	storage modulus ( $E'$ ) at $-75$ °C (MPa)	storage modulus ( $E'$ ) at $100$ °C (MPa)
C60E40	5.2	2720	27.8
C60E40/0.5	5.7	3557	42.6
C60E40/1.5	11.6	3715	58.9
C60E40/2.5	10.8	3719	76.1
C60E40/3.0	10.9	4556.1	88.5

Table 3. Cure Characteristics of Various CPE/EMA Blend Vulcanizates

samples	$M_L$	$M_H$	$T_{S2}$	$T_{90}$	$\Delta M = M_H - M_L^a$	CRI <sup>b</sup>
C60E40/0.5	0.68	2.08	14.12	25.06	1.4	9.14
C60E40/1.5	0.70	4.46	3.56	8.36	3.76	20.83
C60E40/2.5	0.72	6.75	2.20	7.45	6.03	19.04
C60E40/3.0	0.52	8.45	1.46	7.19	7.93	17.45
C100E0/1.5	2.15	7.61	2.32	7.33	5.46	16.89
COE100/1.5	0.22	2.37	7.33	15.06	2.15	8.59

<sup>a</sup> $\Delta M = M_H - M_L$  refers to the extent of cure. <sup>b</sup>CRI indicates the rate of cure.

(as discussed in the subsequent section) and may consume most of the excess DCP, leaving the EMA phase with fewer cross-linking networks. The storage modulus of polymers much below their  $T_g$  is high enough, which is due to the frozen immobilized polymer chains. The introduction of cross-linking in the blend systems caused an increase in the storage modulus ( $E'$ ) of resulting vulcanizates.<sup>28</sup> This is because of the formation of knots during the cross-linking network formation, which caused immobilization of polymer chains. Furthermore, the storage modulus decreased with increasing temperature, which is due to a decrease in stiffness of the samples at high temperatures. This decrease is sharper in the case of an uncross-linked blend, whereas the addition of even 0.5 wt % DCP caused a dramatic reduction in storage modulus during the glass to rubber transition. This means that the addition of a small quantity of DCP (0.5 wt %) may cause effective cross-linking of both CPE and EMA phases and across their interphases. A further increase in DCP concentration in the vulcanizates resulted in a lesser degree of decrease in  $E'$  values across its glass transition regime.

**2.3. Cure Characteristics.** There are three important factors that have a great impact on the co-cross-linking of elastomer blends: polarity of the two polymers, melt viscosity of the two polymers, and cure rate mismatch factor. A greater difference in values of these three factors of the two polymers causes an improper distribution of curing agents in the elastomeric phases. Imbalance in the distribution of curing agents leads to an uneven CLD, resulting in deterioration of mechanical properties.<sup>29</sup> Both CPE and EMA have similar polarity, and hence, the first factor can be ruled out. Therefore, it is essential to observe the remaining two factors by cure characteristic studies. Cure characteristic studies of all blend samples with varying DCP loadings were carried out. Also, the cure characteristics of pure CPE and EMA with 1.5 wt % DCP concentrations were investigated with the purpose of comparison with the optimized C60E40/1.5 blend system. All information on cure characteristics is provided in Table 3.

The  $M_L$  value refers to torque of the compound in an uncured state, and it indicates the viscosity of a compound at a particular temperature. The melt viscosity of CPE at a curing temperature of 160 °C is higher than that of the EMA copolymer, which may cause the curing agent DCP to preferentially reside in EMA during processing.<sup>30</sup> On the other side, the cure rate of CPE is higher than that of EMA, which results in selective migration of DCP to the CPE phase during curing.<sup>31–33</sup> A balance between the two opposite effects can develop good interfacial adhesion between the two elastomeric phases. The maximum torque value is a measure of the CLD that is shown in Table 3.<sup>34</sup> A precipitous drop in optimum cure time ( $T_{90}$ ) at 1.5 wt % DCP loading from 0.5 wt % loadings with little difference in  $T_{90}$  (scorch time) value of C60E40/2.5 blend suggests optimum peroxide loading.

Besides, the C60E40/1.5 blend has the maximum rate of cure among all other blend samples including pure CPE samples. This may be because of the higher extent of curing and the lowest degree of peroxide degradation at this particular DCP loading, which is supported by the mechanical properties of the vulcanizates. From the above discussion, it can be understood that lower  $T_{90}$  values, higher CRIs, and superior mechanical properties of the C60E40/1.5 blend system are because of the optimum and uniform distribution of cross-linking networks at the elastomeric phases and at their interphases.<sup>34,35</sup> The information from the above discussion on the cure characteristics also supports the co-cross-linking phenomenon in the CPE/EMA blend system as can be understood from the enhanced CRI values compared to those of the neat CPE and EMA.<sup>36–39</sup>

**2.4. Cross-Linking Density.** Cross-linking of elastomers causes an appreciable increase in the elastic modulus, UTS, and hardness, with a reduction in the ultimate elongation. Notably, the chemical nature of cross-links is very crucial as they directly correlate to the physical properties of vulcanizates.<sup>40</sup> For instance, peroxide cross-linking generally results in higher thermal degradation stability and lower compression in comparison to sulfur cross-linking. The CLD is one of the key factors to tailor the physical properties of a vulcanizate as mentioned earlier.

The CLDs acquired from swelling tests for C60E40 blends and their vulcanizates with various DCP concentrations are shown in Figure 3. The overall CLD was found to increase

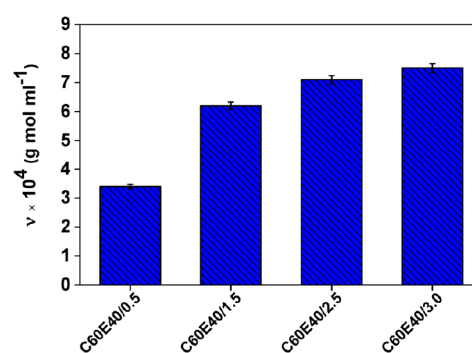
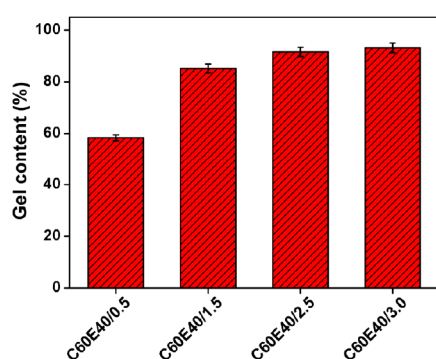


Figure 3. Variation of the overall CLD of various C60E40 blend vulcanizates with varying DCP concentrations.

upon increasing the concentration of DCP in C60E40 blends. The CLD of C60E40/0.5 vulcanizates was pretty low, and the reason could be explained based on the insufficient DCP concentration for network formation. On the other hand, C60E40/1.5 vulcanizates showed an abrupt increase in the CLD, which indicates the effective degree of cross-linking. A further increase in the DCP concentration in the blend did not cause any significant change in the CLD, as it exceeds the

saturation point of cross-linking. Hence, the 1.5 wt % DCP concentration was found to be the optimum quantity for effective cross-linking in the C60E40 blend system. It is worth mentioning that a similar inference has also been drawn from the cure characteristic study of the vulcanizates. The use of excess peroxide quantity in elastomers is not advisable because its catalytic free radical degradation of polymer chains leads to property deterioration. Figure 4 presents the influence of DCP



**Figure 4.** Variation of the gel content of various C60E40 blend vulcanizates with varying DCP concentrations.

concentration on the gel content of the C60E40 blend vulcanizates, which was calculated using eq 2. The gel content of C60E40 vulcanizates was found to increase with increasing DCP concentration, which is in line with the increasing trend of the state of cure as discussed earlier. As an interesting observation, there was a sharp increase in the gel content upon increasing the cross-linking agent (DCP) concentration from 0.5 to 1.5 wt %. When the DCP concentration was more than 1.5 wt %, the gel content eventually flattened. This observation is a clear indication of utmost cross-linking network formation in the C60E40 blend system at 1.5 wt % DCP concentration. DCP above this optimum concentration has little effect on improving the network structure of the blend. This observation is in good corroboration with the noted trend of the calculated cross-link density as well as with the obtained physicochemical properties including the tensile strength, modulus, and % elongation.

**2.5. Cross-Linking Mechanism.** Based on the information extracted from above experiments and literature reports, a plausible mechanism for DCP-initiated cross-linking of the CPE/EMA blend is presented in Scheme 1. The mechanism is thoroughly based on generally accepted reaction steps involved in the process of polymers based on CPE and EMA.<sup>41</sup> At the initial step, peroxide (DCP) undergoes homolytic cleavage, thereby producing cumyloxy radicals. These cumyloxy radicals are highly reactive and unstable and may lead to formation of methyl radicals.<sup>42</sup> These free radicals being highly unstable lead to formation of another covalent bond.

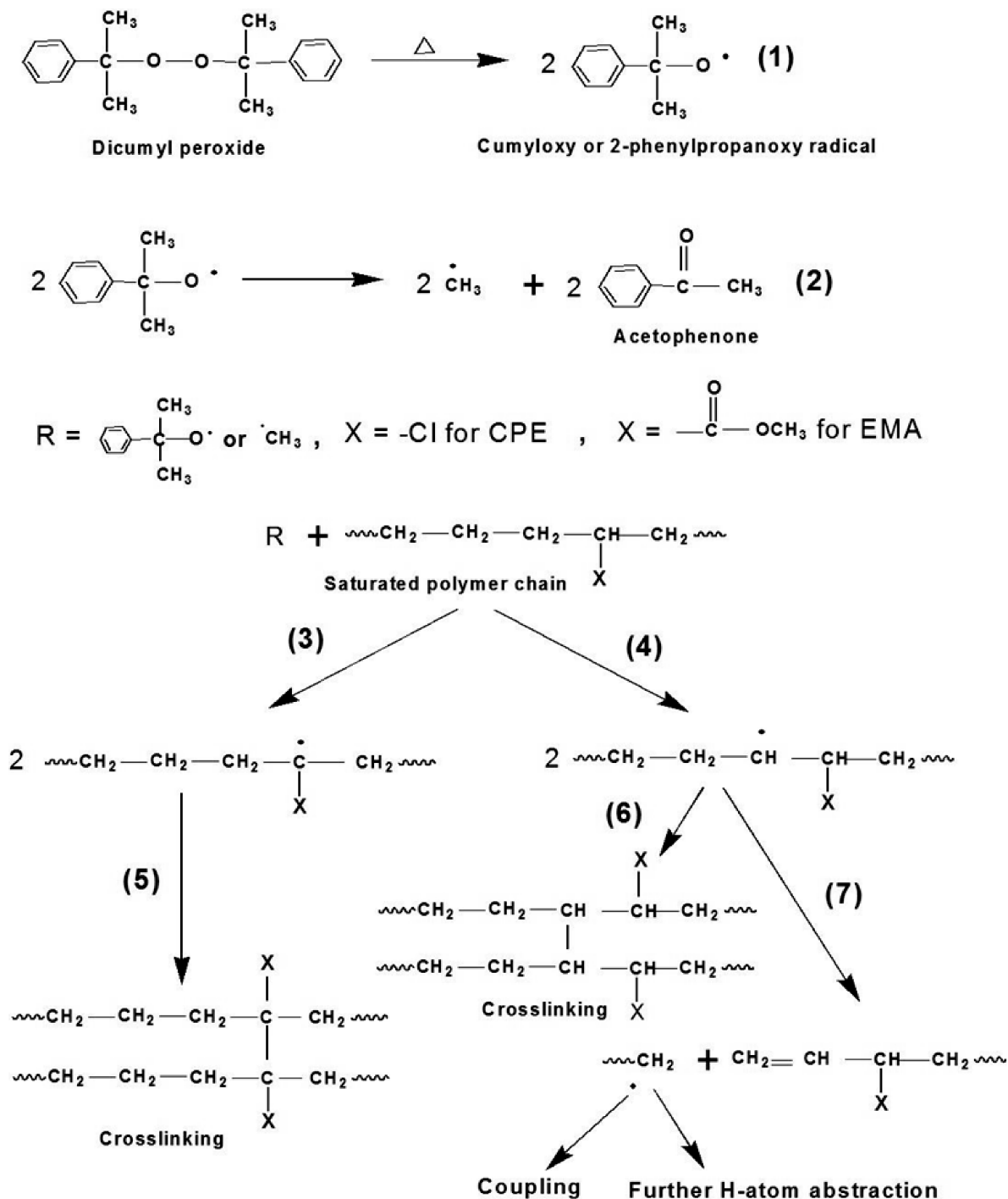
Normally, this step occurs by the abstraction of a labile hydrogen atom from the polymer backbone chains, which further leads to the development of free radicals on the polymer chain backbone. Coupling among these hydrocarbon radicals of the polymer chain leads to cross-linking of polymers, which is predominant over some other side reactions due to the lower activation energy required. The plausible peroxide cross-linking reactions of saturated polymers based on various kinds of literature works are presented in Scheme 1.<sup>36,43</sup> In the DCP cross-linking phenomenon, the methyl and

2-phenylpropanoxy radicals acted as the major reactive species for the cross-linking reaction.<sup>44</sup> The DCP cross-linking mechanisms of ethylene-based polymers have received significant importance not only due to the rate of reaction but also because of the high degree of chemical conversion.<sup>42</sup>

**2.6. SEM Analysis.** SEM is one of the reliable techniques that is generally performed to justify the results obtained from physical data and physicochemical properties.<sup>45</sup> An attempt was made to selectively etch out the EMA phases from CPE/EMA vulcanizates using suitable solvents, but there was no change in the morphology. It is worth mentioning here that in our previous work, selective etching out of the EMA phase led to evolution of droplet morphology of the uncured CPE/EMA blends. To attain a better understanding of the surface morphology of the vulcanizates, cryofractured surfaces were examined under a scanning electron microscope (SEM) in the present study. The pictorial evidence renders better insight into the morphology of the peroxide-cured CPE/EMA blend of 60:40 ratio. Figure 5 shows photomicrographs of cryofractured samples, which depict self-evident predominant surface textures. Figure 5a represents the cryofractured morphology of C60E40/0.5, which contains plenty of voids with a shattered surface. This indicates the absence of sufficient interface adhesion between the two rubbers. The reason could be due to insufficient quantity of peroxide to cure the two elastomeric phases efficiently. This may also lead to inefficient curing of the interfaces of two elastomers. Furthermore, the C60E40/1.5 blend system has a much higher degree of compactness that can be realized by observing strong ridgelines as in Figure 5b. This compact nature of the blend system is reflected in the mechanical property improvement. The chemical reaction among phases initiated by DCP occurred across the interface, which reduced the interfacial tension. However, as shown in Figure 5c,d, a further increase in the DCP loading in the blend showed the presence of a lot of debris along with some voids. The reason for such morphology is an excess DCP content that resulted in a cure mismatch in the two elastomeric phases. The higher peroxide loading may cause its improper migration and poor solubility in the respective polymer matrix or blend during processing (melt mixing). The excess of peroxide may cause overcuring of the CPE phase, which has a higher cure rate than EMA. The poor interfacial interaction between the two elastomeric phases is a direct consequence of cure mismatch. This lack of coherency in the blend morphology is corroborated with the decreased mechanical properties of C60E40/2.5 and C60E40/3.0 vulcanizates.

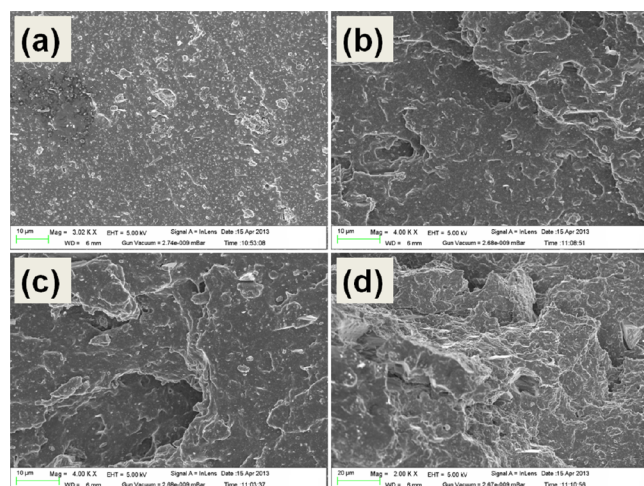
**2.7. Thermogravimetric Analysis (TGA) Studies.** TGA has proved to be one of the finest tools to study thermal degradation stability of polymeric materials.<sup>46</sup> In the area of product development and applications, the knowledge of thermal degradation stability of polymeric systems is highly recommended.<sup>47</sup> The effect of peroxide concentration on the thermal stability of the C60E40 blend and its vulcanizates was investigated using a thermogravimetric analyzer. Here, a comparative study of un-cross-linked C60E40 blends and their peroxide vulcanizates was carried out. The TGA and corresponding DTG graphs are shown in Figure 6a,b. Figure 6 displays two steps of degradation of weight loss of both un-cross-linked and cross-linked blend systems. The first step is at around 300 °C, and the second step is above 450 °C. The first step of degradation is due to the dehydrochlorination of the chlorine present in the CPE backbone, while the second step is

Scheme 1. Plausible Cross-Linking Mechanism of CPE and EMA Using DCP



due to the beginning of polymer degradation and polyene formation. Characteristic information determined by the TGA and DTG analyses of the blends and their vulcanizates is summarized in Table 4. The initial degradation temperature ( $T_i$ ) of the blends belongs to 1% degradation, which was obtained from the TGA plot, and a higher  $T_i$  value means higher thermal stability. The blend that has 1.5 wt % DCP concentration (C60E40/1.5) showed the highest  $T_i$  value compared to other vulcanizates and un-cross-linked blends. The addition of an optimum quantity of DCP (1.5 wt %) in the C60E40 blend resulted in favorable interactions at the interface through cross-linking. Thus, the interfacial tension

decreased, which enhanced the thermal degradation stability of the blend vulcanizates, and this correlation supports the superior mechanical properties of the blend vulcanizates as discussed in the earlier section.<sup>48</sup> A further increase in the DCP concentration in the blend caused an increase in the rate of degradation as can be assessed from the increase in  $T_{50\%}$  values Figure 6(b). The reason for such an increase in the rate of degradation in C60E40/2.5 and C60E40/3.0 is possibly due to the formation of shorter polymer chains during cross-linking. Additionally, an excess amount of DCP may cause chain scission in the polymer backbone during curing. Furthermore, there is a possibility of unconsumed peroxides



**Figure 5.** SEM photomicrographs of cryofractured: (a) C60E40/0.5, (b) C60E40/1.5, (c) C60E40/2.5, and (d) C60E40/3.0 blend vulcanizates.

selectively migrating toward CPE (with high CRIs) over EMA. This may lead to less interphase cross-linking and low CLD in the EMA phase, which may have accelerated the thermal degradation. Hence, it can be understood that the blend C60E40 with the optimum DCP content of 1.5 wt % showed improved thermal degradation stability due to more network formation at the interfaces. However, the vulcanizates with higher DCP concentrations have higher residue contents, which is obviously because of higher CLDs.

**2.8. Oil and Flame Resistance and Electrical Properties.** **2.8.1. Oil Resistance Test.** Table 5 displays the effect of DCP concentration on oil swelling resistance of CPE/EMA blends and their vulcanizates in ASTM D #3 oil at ambient temperature for 7 days. According to Mousa et al.,<sup>49</sup> the osmotic pressure of the solvent (in the present case, it is ASTM D #3 oil) is the driving force that leads to swelling of mass.<sup>49</sup> When the osmotic pressure of the solvent is higher than inter- and intramolecular bonding of CPE/EMA blends, swelling occurs. In our present investigation of oil resistance, an effective degree of improvement in C60E40/0.5 was observed compared to that of un-cross-linked C60E40 blends.

**Table 4.** Parameters Extracted from Thermograms and Derivative Thermograms of C60E40 Blends and Their Vulcanizates

sample designation	initial decomposition temperature ( $T_i$ ) (°C)	temperature at 50% weight loss ( $T_{50\%}$ ) (°C)	residue content (wt %)
C60E40	293.2	474.7	5.3
C60E40/0.5	294.4	476.1	9.4
C60E40/1.5	299.4	479.4	10.4
C60E40/2.5	298.9	479.1	11.4
C60E40/3.0	291.5	477.8	13.3

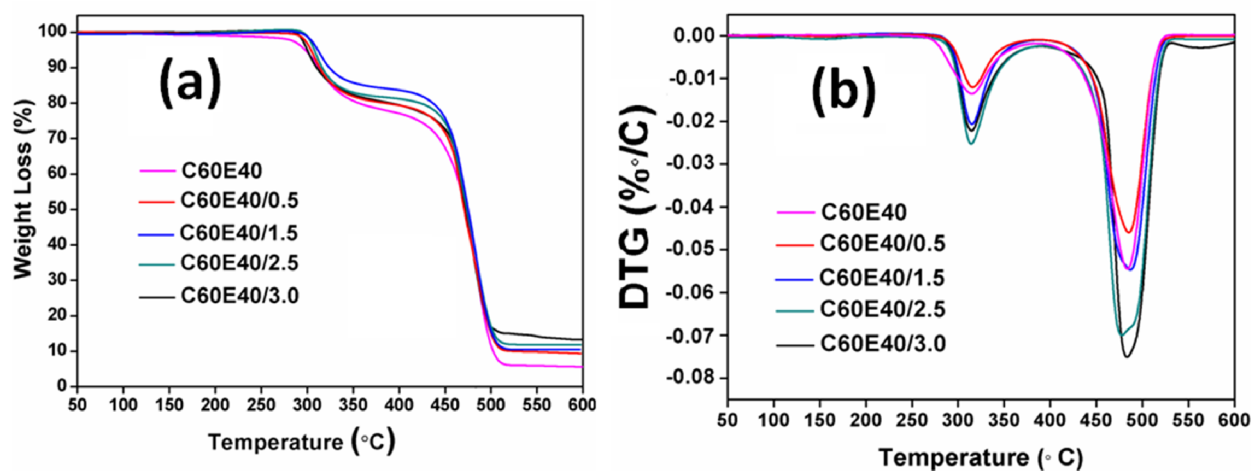
**Table 5.** Oil and Flame Resistance Characteristics of Neat Blends and Their DCP Vulcanizates

sample designation	oil swelling ratio (Q%)	LOI
C60E40	4.61	23 ± 0.3
C60E40/0.5	4.06	23 ± 0.5
C60E40/1.5	3.52	25 ± 0.7
C60E40/2.5	2.94	24 ± 0.3
C60E40/3.0	2.88	24 ± 0.2

However, a remarkable increase in the oil resistance property was observed in the case of C60E40/1.5 and C60E40/2.5 due to the existence of an adequate number of cross-linking networks in the respective blend vulcanizates. At a higher CLD, the molecular weight between two adjacent cross-links decreases, and consequently, the osmotic pressure of oil also reduces.<sup>50</sup> The poor osmotic pressure of oil naturally led to a reduction in the diffusion of oil into the CPE/EMA blends.

However, a further increase in DCP concentration did not cause any improvement in the oil resistance property of the C60E40 blends. Rather, the oil resistance of C60E40/3.0 was seemingly almost equivalent to that of the C60E40/2.5 blend system due to the saturated degree of cross-links even at high DCP concentrations. Hence, DCP cross-linking at its optimum concentration (1.5%) improved the oil resistance property of CPE/EMA blend vulcanizates efficiently.

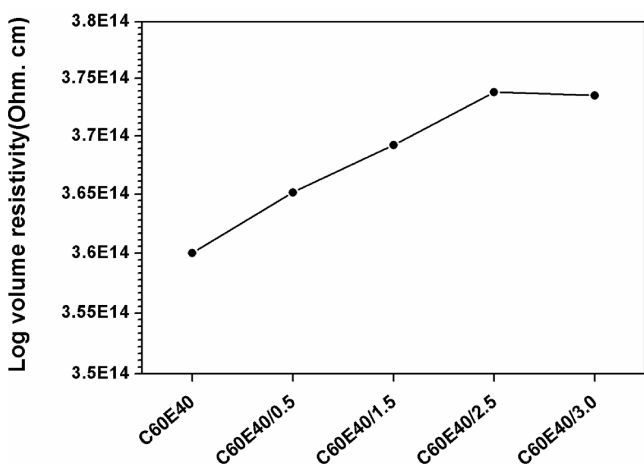
**2.8.2. Limiting Oxygen Index (LOI) Test.** The flame resistance characteristics of DCP-cross-linked C60E40 blend vulcanizates were studied by the LOI test. The effect of DCP concentration on the C60E40 blend system was understood by



**Figure 6.** Thermal stability of un-cross-linked and cross-linked C60E40 blend vulcanizates. (a) TGA plots and (b) derivative thermogravimetric plots.

comparing the LOI values with the un-cross-linked C60E40 blend, and the obtained data are tabulated in Table 5. All DCP cross-linked samples showed higher LOI values compared to that of un-cross-linked C60E40 blends. Besides, increasing DCP concentration in the formulation also caused a simultaneous increase in LOI values due to network formation at the interfaces. Moreover, the improved thermal stability of three-dimensional cross-linked network structures is also responsible for the higher LOI values.

**2.8.3. Volume Resistivity.** Figure 7 showing the room-temperature volume resistivity of the un-cross-linked C60E40



**Figure 7.** Volume resistivity of un-cross-linked and cross-linked C60E40 blend vulcanizates.

blend and its peroxide cross-linked blend systems with various DCP concentrations. All cross-linked systems showed higher volume resistance than the C60E40 blend. Besides, the volume resistance kept on increasing with increasing DCP concentration in the blend. The volume resistivity of polymers is associated with the density of cross-linking networks caused by peroxide cross-linking. The cross-linking knots act as barriers to restrict the movement of electrical charges. However, the increment in volume resistivity of cross-linked systems showed a marked increase up to 1.5 wt % DCP. A further increase in DCP concentration did not cause any significant improvement in volume resistivity. This may be due to the possible degradation of polymer chains caused by the excessive peroxide-initiated free radicals.

### 3. MATERIALS AND METHODS

**3.1. Materials.** Commercial-grade CPE elastomer (CPE 360) having 36% chlorine content, a density of 1.213 g cm<sup>-3</sup>, and Mooney viscosity of 65 ± 5 at ML<sub>(1+4)</sub> at 121 °C was generously gifted by East Corp International, India. EMA, copolymer, of grade Elvaloy 1330, which has 30% methyl acrylate and a melt flow index of 3 g 10 min<sup>-1</sup> (at 190 °C/2.16 kg) with a melting point of 85 °C was gifted by NICCO Corporation, Shyamnagar, India. Dibutyltindilaurate and Irganox 1010 were purchased from Sigma-Aldrich and used as heat stabilizers and antioxidants, respectively, for processing of CPE elastomers. DCP was used as a curing agent for the processing of polymer blends.

**3.2. Methods.** **3.2.1. Preparation of Blends and Their Vulcanizates by the Melt Mixing Approach.** DCP is used as a curing agent with the concentrations of 0.5%, 1.5%, 2.5%, and

3% of total base blend formulations combined with other ingredients. The blend ratio of the CPE and EMA polymer was kept constant as 60:40 (C60E40), and it was fabricated by the typical melt mixing route using a HaakeRheomix internal mixer at 140 °C mixing temperature for 14 min with 60 rpm speed of the rotor. In melt mixing, first CPE was softened for 2 min along with other ingredients such as MgO, DBTDL, and Irganox 1010. Upon mixing of the above ingredients, EMA was incorporated into it and mixing was continued for 6 more minutes. Thereafter, DCP was added to the above mixtures for cross-linking and mixing was continued for extra 6 min. Finally, the mixed blend lumps were collected and sheeted out using two roll mills. All of the molded sample slabs were cooled under tap water and then conditioned for 24 h before characterization. The sample designations of prepared un-cross-linked and cross-linked CPE/EMA blends are mentioned in Table 6.

**Table 6. Sample Designations and Their Composition<sup>a</sup>**

sample designation	CPE	EMA	DCP (wt %)
C60E40/0	60	40	0.0
C60E40/0.5	60	40	0.5
C60E40/1.5	60	40	1.5
C60E40/2.5	60	40	2.5
C60E40/3.0	60	40	3.0

<sup>a</sup>All other ingredients MgO, DBTDL, and Irganox 1010 are of 3, 1, and 1 phr, respectively, w.r.t. both polymers.

**3.2.2. Characterization Techniques.** **3.2.2.1. Mechanical Properties.** The mechanical property under tensile mode was determined by following ASTM D 412-98 at a typical strain rate of 500 mm min<sup>-1</sup> using a Hioks-Hounsfield Universal Testing Machine, Surrey, England. Shore A hardness was tested for the prepared blends by following ASTM D2240 in Rex-2000, Buffalo Grove, USA.

**3.2.2.2. Dynamic Mechanical Analysis.** Dynamic mechanical properties of the fabricated blends were evaluated using DMA Q800 (TA Instruments, Lukens Drive, Newcastle, DE) under tension mode in the dynamic temperature range from -100 °C to +100 °C at a heating rate of 3 °C min<sup>-1</sup> along with 0.1% constant strain and 1 Hz frequency.

**3.2.2.3. Cure Characteristics.** The cure properties of blends were evaluated by an oscillating disk rheometer (ODR) at a temperature of 160 °C with an oscillation degree of 3°. The blends were cured up to their optimum cure time (90% of the maximum cure) obtained from the ODR rheograph at a pressure of 7 MPa at the same temperature. Approximately, about 10 g of samples was placed between the upper and lower discs, and a test was performed to obtain the optimum cure time for each sample.

**3.2.2.4. Cross-Linking Density.** The CLD of vulcanized blend samples was evaluated from the equilibrium swelling testing of the toluene solvent at ambient temperature for 7 days. From the degree of swelling from the equilibrium swelling testing, the CLD of cross-linked blends was determined by applying the Flory-Rehner equation as follows:

$$\nu = -\frac{1}{V_r} \times \frac{\ln(1 - V_r) + V_r + \chi \times V_r^2}{V_r^{1/3} - 0.5V_r} \quad (1)$$

where  $\nu$  is the number of moles of elastic chains per unit volume of the polymer [mol mL<sup>-1</sup>], i.e., CLD,  $V_s$  is the molar



volume of toluene ( $\text{cm}^3 \text{mol}^{-1}$ ), and  $\kappa$  is the Flory–Huggins interaction parameter (about 0.454) at ambient temperature as obtained from the literature.<sup>51</sup> However,  $V_r$  is the volume fraction of the polymer in the swollen network and  $V_r$  can be calculated by the method of Ellis and Welding as follows:<sup>52</sup>

$$V_r = \frac{(d - f_w) \rho_r - 1}{(d - f_w) \rho_r - 1 + A_s \rho_s^{-1}} \quad (2)$$

where  $d$  is the deswollen weight of the specimen,  $A_s$  is the amount of toluene absorbed,  $f_w$  is the volume fraction of insoluble components, and  $\rho_r$  and  $\rho_s$  are the densities of the polymer and the solvent (toluene), respectively.

**3.2.2.5. Gel Content Studies.** The gel contents of DCP cross-linked blends were evaluated using a Soxhlet extraction method. First, cross-linked C60E40 blends were extracted with chloroform solvent for about 48 h. Subsequently, the extraction was continued by chlorobenzene solvent at its boiling point for about 48 h. Triplicates were followed for each cross-linked blend sample, and the final extracted blends were dried in an oven at 60 °C until a constant weight was obtained. The percentage gel content was obtained using the following empirical equation:

$$\text{gel (\%)} = \frac{W_1}{W_2} \times 100 \quad (3)$$

where  $W_1$  and  $W_2$  are the weight of the dried blend sample after extraction and the weight of the blend sample before extraction, respectively.

**3.2.2.6. Scanning Electron Microscopy (SEM).** Surface morphologies of various cryofractured (fractography) blends and their vulcanizates were examined using a SEM (model Zeiss EVO 60, Carl Zeiss SMT, Germany) at an operating voltage of 20 kV. The gold coating was also performed on the surface of all of the samples before exposing them under a microscope.

**3.2.2.7. TGA Studies.** Thermal stabilities of various blends and their vulcanizates were evaluated using a TGA STARE system, METTLER TOLEDO, at a heating rate of 20 °C  $\text{min}^{-1}$ . TGA was performed under a nitrogen atmosphere (inert) in the temperature range between 45 and 600 °C.

**3.2.2.8. Oil Resistance Test.** The oil resistance characteristics were also tested by the oil swelling test using ASTM #3 oil according to the ASTM D 471-06 standard. ASTM #3 oil was used to measure oil resistance characteristics of various blends and their vulcanizates at ambient temperature for 72 h. The percentage swelling ratio,  $Q\%$ , was measured using the following empirical equation:

$$Q\% = \frac{W_2 - W_1}{W_1} \quad (4)$$

where  $W_2$  and  $W_1$  denote weights after and before swelling of blends and vulcanizates in oil, respectively.

**3.2.2.9. Flame Resistance Test.** The flame resistance of the prepared blends and their vulcanizates was evaluated by measuring the LOI as LOI is the minimum concentration of oxygen (%) in a mixture of oxygen and nitrogen that needed to ignite the blend samples at ambient temperature. LOI was performed by following ASTM D 2863-77 using a flammability tester (SC Dey Co., Kolkata). The volume ratio between nitrogen and oxygen gases at which the blend samples begin to

burn was recorded for at least 30 s. The percentage LOI was measured using the following empirical equation:

$$\text{LOI} = \frac{\text{volume of O}_2}{\text{volume of O}_2 + \text{volume of N}_2} \times 100 \quad (5)$$

**3.2.2.10. Volume Resistivity Measurement.** The DC volume resistivity of the prepared blends and their vulcanizates were evaluated using a Hewlett Packard 4339B (High Resistance Meter coupled with Agilent 16008B Resistivity Cell, Japan) at ambient temperature by applying 500 V. Subsequently, the volume resistivity was also measured using the following empirical equation as per ASTM D 257-66

$$\text{volume resistivity } (\Omega \text{ cm}) = \frac{A \times R}{t} \quad (6)$$

where  $A$  is the area of the upper electrode (19.6  $\text{cm}^2$ ),  $R$  is a resistance (ohm) between upper and lower electrodes, and  $t$  is the thickness (cm) of the test blend samples.

## 4. CONCLUSIONS

A systematic study was carried out to investigate the effect of DCP cross-linking of CPE/EMA blends with a 60:40 ratio (C60E40) with special reference to their DCP concentrations on technical properties such as mechanical, thermal, and electrical. Modification of C60E40 blends with DCP by the cross-linking route showed appreciable improvement in static and dynamic mechanical properties, thermal stability, oil and flame resistance, and enhanced volume resistivity. Among all, the vulcanizate C60E40/1.5 showed 78% increment in the UTS and storage modulus and outstanding thermal stability compared to those of un-cross-linked (C60E40) blends and other cross-linked blend vulcanizates. The effective cross-linking in CPE and EMA phases across their interphases is reflected in marginal improvement of mechanical and thermal properties of C60E40/1.5 blend vulcanizates. This signifies that the 1.5 wt % DCP concentration is the best and the optimum peroxide loading for C60E40 blends. The surface morphology study of the cryofractured blend vulcanizates by SEM analysis reveals a higher degree of compactness as realized by the observation of strong ridgelines in C60E40/1.5 vulcanizates. On the other hand, C60E40/2.5 and C60E40/3.0 exhibited a large number of microvoids and poor compactness, which indicates improper interphase cross-linking at higher DCP concentrations. The peroxide cross-linking route also demonstrated a positive influence on oil resistance and flame resistance characteristics of C60E40 blends, and a similar increasing trend in volume resistivity was also noticed with increasing DCP concentration in the blend vulcanizates. Taken together with all of the results, the present investigation will be helpful for cable industry applications, where mechanical and thermal properties are important along with electrical properties.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c01727>.

Dynamic mechanical properties (storage modulus and  $\tan \delta$ ) of CPE and EMA cured with 1.5% DCP (PDF)

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## Notes

The authors declare no competing financial interest.

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