Property Deterioration in Reactive Elastomeric Terpolymer Modified Binders During Storage at Elevated Temperatures

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Research Article

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Abstract

Polymer-modified binders are often stored and transported at elevated temperatures, where their properties may deteriorate if mishandled. This study investigates the effect of storage temperature, storage time, base binder, and PPA concentration on the conventional and rheological properties of commercial-grade reactive elastomeric terpolymer-modified binders (RET-MBs). To mimic practical storage conditions, RET-MB was contained in sealed metal tubes and stored in a forced convection oven at temperatures of 120, 135, 150, and 165°C for up to 14 days. The results show that the deterioration in conventional and rheological properties of RET-MB was noticeable even at a low storage temperature of 135°C. At temperatures of 150 and 165°C, significant erosion in properties was observed within the first three days of storage. After 7 days of storage at 150°C, the softening point, $T_u$, and % elastic recovery values decrease by 4°C, 3.5°C, and 46%, respectively. One PG-grade drop can occur after 3–7 days of storage at 150 and 165°C. FTIR analysis of the solution-cast films of RET polymer reveals a strong interaction of the epoxy ring with PPA molecules to form phosphate ester linkage during storage, due to which the interaction between RET polymer and binder molecules reduces, resulting in property erosion during storage. The results show that RET-MBs should be stored and transported at temperatures < 135°C.

1. Introduction

Increased traffic volume, axle loads, extreme weather conditions, etc., are causing early failures in asphalt pavements [1, 2]. Asphalt pavements performance can be enhanced using polymer-modified binders (PMBs) [3–7]. Commercially, reactive elastomeric terpolymers (RET), such as ethylene-butyl acrylate-glycidyl methacrylate (EnBAGMA), ethylene-methyl acrylate-glycidyl methacrylate (EMGMA), etc., are widely used to modify asphalt binders [3, 4]. RET is the general term used for ethylene-based copolymers consisting of an acrylate (usually methyl, ethyl, or butyl acrylate) and a glycidyl methacrylate (GMA) unit [1, 8].

The GMA unit’s highly reactive and polar epoxy ring acts as a compatibilizer between the RET polymer and the binder molecules [3, 9, 10]. The epoxy ring in the GMA unit interacts with carboxylic, hydroxyl, or amine groups in the asphalt binder [7]. This interaction prevents phase separation of the RET molecules during storage at elevated temperatures ($\geq 100^\circ$C) [11]. Once the epoxy ring has reacted, intermolecular crosslinking can occur between the polymer molecules under heat and pressure [3]. RETs are generally used along with polyphosphoric acid (PPA), a liquid mineral polymer used to enhance the properties of paving-grade asphalt binder. PPA increases the stiffness of the binder and the interaction between the epoxy ring in the RET polymer and asphalt binder molecules [5, 6, 12, 13]. Commercially, the concentration of the RET polymer in the binder is generally kept below 2.5 wt.%, as gelling is observed at higher dosages [3, 14]. RET modification of asphalt binder improves properties like softening point, penetration, and percent elastic recovery [8, 15, 16]. The asphalt mixes based on RET-MB enhance mix properties like sensitivity to moisture damage, rut performance, and marshal stability [17].

Commercially, PMBs are exposed to elevated temperatures (120°C–180°C) during storage and transportation in closed metal containers where the presence of air is limited. PMBs are generally stored and transported at temperatures > 120°C because reheating them is difficult and time-consuming if stored at very low temperatures. Various organizations and PMB suppliers provide storage and handling guidelines to prevent
property deterioration during storage and transportation [18–20]. Several studies have analyzed the effect of elevated storage conditions in styrene-butadiene-styrene modified binders (SBS-MB) and asphalt mix based on such binders [21–24]. The properties of SBS-MB deteriorated severely at a storage temperature of 180°C due to the degradation of the SBS polymer molecules.

However, no systematic study has been carried out to evaluate the effect of elevated temperature storage on the performance properties of RET-MBs. Hence, no specific storage and handling guidelines are currently available for RET-MBs. In the present study, we focus on the effect of storage parameters (time and temperature of storage), base binder, polymer type, and PPA concentration on the conventional and rheological properties of RET-MBs. At a constant RET content of 2 wt.%, PPA content, base binder, and polymer type were varied. To simulate the commercial storage conditions of binders, RET-MBs were stored in sealed metal tubes at different temperatures (120, 135, 150, and 165°C) for up to 14 days [25]. This comprehensive study demonstrates the importance of having specific storage and handling guidelines for RET-MBs, thereby helping commercial manufacturers and pavement engineers.

2. Materials and Methods

2.1 Materials:

The details of the source and properties of the selected binders (B₁, B₂), selected RET polymers (RET₁, RET₂), and polyphosphoric acid (PPA) are given in Table 1. The study used two asphalt binders from different sources and penetration grades (85/100 and 60/70). Although the spread in the binder samples is limited (supplier and properties), it will help us to know if the base binder plays a major role in governing the properties of RET modified binders (RET-MB) during storage. Polyphosphoric acid (PPA) (Hₙ₊₂PₙO₃n₊₁) is used to enhance the interaction within the RET-binder system [5, 26]. It is an inorganic oligomer obtained by condensing the mono-phosphoric acid (H₃PO₄) or hydration of phosphorus pentoxide (P₂O₅) [11].

The two commercial-grade RET polymers utilized as modifiers are ‘Elvaloy® 4170’ (RET₁) and ‘Elvaloy® 5170’ (RET₂), and they are reported to be highly reactive by the supplier. Comprehensive analysis was carried out using the RET₁ polymer as it is extensively used commercially, while RET₂ polymer was used to ascertain the effect of changes in the RET polymer composition. RET₁ is an E-nBA-GMA (ethylene-n-butyl acrylate-glycidyl methacrylate) terpolymer, while RET₂ is an E-E-GMA (ethylene-ester-glycidyl methacrylate) terpolymer [27]. 1H NMR confirms the presence of n-butyl acrylate and vinyl acetate units in RET₁ and RET₂, respectively. The glycidyl methacrylate content in both the polymers is around 7–9 wt.%. Figure 1 presents the chemical structure and Fourier transform infrared (FTIR) spectra of RET₁ carried out in attenuated total reflectance (ATR) mode between 2000 – 600 cm⁻¹. The RET₁ is subjected to Soxhlet extraction for 1-1.5 hrs. using toluene as a solvent to remove the various additives and stabilizers present in the polymer before carrying out its FTIR.

It is important to note that the ester group (RCOOR') is present both in butyl acrylate/vinyl acetate and GMA, while the epoxy ring (C₂H₃O) is present only in GMA. In RET polymer, it is essential to analyze the FTIR peaks associated with the epoxy ring and ester group, as they offer potential sites of interaction with the asphalt binder [8]. The peaks near 1168, 1065, and 1640 cm⁻¹ correspond to the C-O stretch of ester group. The peak
near 910 cm\(^{-1}\) corresponds to the GMA moiety’s epoxy ring, and its strength decreases as the curing of epoxy ring proceeds [28–31]. The peaks near 1732 cm\(^{-1}\) correspond to the carbonyl group of ester functionality. The peaks of aliphatic groups appear near 1466, 1380 and 721 cm\(^{-1}\), corresponding to the CH\(_3\) asymmetrical, symmetrical bending vibrations and CH\(_2\) rocking vibrations respectively. The epoxy ring is highly reactive and improves the interaction capability of the RET polymer. However, it is essential to note that the FTIR peaks associated with the epoxy ring are weak due to the lower content of GMA in the RET polymers and only 2 wt.% RET is used to modify the binder.
## Table 1
Properties of the selected asphalt binders, RET polymers, PPA, and properties of RET-MBs as a function of PPA concentration, base binder, and RET polymer

<table>
<thead>
<tr>
<th>Binder</th>
<th>Source</th>
<th>Pen. @ 25°C (dmm)</th>
<th>Soft. Point (°C)</th>
<th>Absolute Vis. @ 60°C (Poise)</th>
<th>PG Upper Temp. (°C)</th>
<th>RTFO aged Retained Pen (%)</th>
<th>Vis. ratio @ 60°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>B₁</td>
<td>Indian Oil-Total</td>
<td>94</td>
<td>48</td>
<td>1200</td>
<td>1200</td>
<td>52</td>
<td>2.8</td>
</tr>
<tr>
<td>B₂</td>
<td>Tiki Tar-Shell</td>
<td>66</td>
<td>53.6</td>
<td>1340</td>
<td>1340</td>
<td>54</td>
<td>2.6</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>RET polymer</th>
<th>Polyphosphoric acid</th>
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</thead>
<tbody>
<tr>
<td>Nomenclature</td>
<td>RET₁, RET₂</td>
</tr>
<tr>
<td>Commercial grade</td>
<td>Elvaloy 4170, Elvaloy 5170</td>
</tr>
<tr>
<td>Supplier</td>
<td>Sigma Aldrich, Reagent Grade</td>
</tr>
<tr>
<td>Density, g/cc</td>
<td>0.94, 0.94</td>
</tr>
<tr>
<td>MFI, g/10min</td>
<td>8, 8</td>
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<tr>
<td>Melting Point, °C</td>
<td>72, 82</td>
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<tr>
<td>Max Processing Temp., °C</td>
<td>310, 220</td>
</tr>
<tr>
<td>GMA content, %</td>
<td>9, -</td>
</tr>
<tr>
<td>Density, g/mL @ 25 °C</td>
<td>2.06</td>
</tr>
</tbody>
</table>

### RET-MB

<table>
<thead>
<tr>
<th>Variable</th>
<th>Sample</th>
<th>SP (°C)</th>
<th>T_u (°C)</th>
<th>ER @ 60°C (%)</th>
<th>Vis. @ 150°C (Pa.s)</th>
<th>Δ SP (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPA Content</td>
<td>B₁-2%RET₁-0%</td>
<td>63.4</td>
<td>65.2</td>
<td>28</td>
<td>0.82</td>
<td>1.2</td>
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<tr>
<td></td>
<td>B₁-2%RET₁-0.1%</td>
<td>65.8</td>
<td>71.5</td>
<td>62</td>
<td>0.85</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>B₁-2%RET₁-0.2%</td>
<td>67.6</td>
<td>73.5</td>
<td>80</td>
<td>1.17</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>B₁-2%RET₁-0.3%</td>
<td>72.2</td>
<td>74.6</td>
<td>81</td>
<td>1.2</td>
<td>0.4</td>
</tr>
<tr>
<td>Binder (B₂)</td>
<td>B₂-2%RET₁-0.2%</td>
<td>79.0</td>
<td>95.1</td>
<td>100</td>
<td>2.50</td>
<td>0.6</td>
</tr>
<tr>
<td>Polymer (RET₂)</td>
<td>B₁-2%RET₂-0.2%</td>
<td>66.4</td>
<td>70.0</td>
<td>55</td>
<td>1.10</td>
<td>0.6</td>
</tr>
</tbody>
</table>

### 2.2 Test methods:
Conventional tests such as penetration, softening point, absolute viscosity at 60°C, and Brookfield viscosity at 150°C were carried out as per ASTM D5, ASTM D36, ASTM D2171, and ASTM D4402, respectively. The phase stability of the RET-MBs was determined as per ASTM D7173. The rheological characterizations were performed in the linear viscoelastic (LVE) region using a dynamic shear rheometer (DSR) as per ASTM D7175. For determining the PG upper limiting temperature ($T_{u}$), the $|G^*|/\sin\delta$ parameter was measured at an angular frequency ($\omega$) of 10 rad/s in the LVE region, as per ASTM D6373. The % elastic recovery (% ER) values of the fresh and stored RET-MBs were determined through a multi-stress creep and recovery (MSCR) test at 60°C, as per ASTM D7405. The average % ER value from 10 creep and recovery cycles is reported in this study. Additionally, frequency sweep measurements from 0.01 to 10 rad/s were performed in the LVE region at 10% strain to comprehensively evaluate the effect of storage on the rheological properties of the RET-MBs.

FTIR spectrum was analyzed between 2000 – 600 cm$^{-1}$ wave number in ATR mode to evaluate the response from binders and RET polymers. Gel permeation chromatography (GPC) instrument was used to determine the changes in molecular weight and molecular weight distribution of binder components (asphaltene, maltene). The instrument had an SEC/3010 pump and a refractometer detector. Tetrahydrofuran (THF) used as a solvent for preparing binder solution of concentration 10 mg/ml. The solution was injected into the column at 30°C, and a 1 ml/min solvent flow rate was maintained.

### 2.3 Preparation of RET-modified binders (RET-MB):

RET-MB was prepared according to the guidelines provided by the polymer manufacturing company [32]. The asphalt binder was heated to 180–185°C in a tin container, and the required amount of RET polymer was added to the liquefied asphalt binder. IKA-Werke low shear mixer (Model: RW20) was used for homogeneous mixing of the RET polymer at 700 rpm for 4 hrs. The required amount of PPA was added 30 minutes before mixing was completed to accelerate the interaction between the asphalt binder and RET polymer. The RET-MB was then stored for 12 hrs. inside a forced convection oven at 150°C for proper stabilization and completion of reactions within the binder-RET-PPA system [6].

Properties of the 6 RET-MBs as a function of PPA dosage (0, 0.1, 0.2, and 0.3 wt.%), base binder ($B_1$ and $B_2$), and polymer ($RET_1$, $RET_2$) are given in Table 1. The property enhancement is evident with increasing the PPA dosage in Table 1. PPA increases the stiffness of the base binder, and also enhances the interaction between the RET polymer and base binder. The concentration of RET polymer in asphalt binder should not exceed 2.5 wt.%, as at higher dosages, the RET tends to form an infusible and insoluble mass or gel. The optimum content of RET polymer is selected as 2 wt.% for this study. The base binder also strongly influences the properties of the RET-MBs; hence, studies were carried out as a function of base binders ($B_1$ and $B_2$). Since the $B_2$ binder was stiffer than $B_1$, the properties of the RET-MB prepared using $B_2$ were higher than the $B_1$ base binder at a fixed RET and PPA content. The type of RET polymer ($RET_1$ and $RET_2$) at a fixed PPA dosage influences the modified binders differently, as evident from Table 1. The $RET_1$ modified binder exhibits superior properties, especially the %ER.

### 2.4 Storage protocol:

Factors like type of storage/transportation containers (shipping containers, metal drums etc.), heating system (oil and flame), the location of the PMB manufacturing plant and the customer site, and road construction...
scenarios govern the duration of exposure to elevated temperatures. As per existing industrial practice, after manufacturing, the polymer modified binders (PMBs) are stored in metal containers between 120°C to 150°C when the application time is after one week. If the PMBs are to be used within one week, they are usually stored at temperatures between 150°C and 180°C [19, 20, 33]. In our study, considering commercial scenarios, the temperatures of storage were selected to be 120, 135, 150, and 165°C. Commercially, it is unlikely to store RET-MBs for more than 2 weeks at 165°C, so the storage duration was limited to 14 days. After preparation, around 120 g of RET-MBs was poured into aluminum storage tubes of 180 mm length x 35 mm diameter. The open end of the tube was closed tightly so that the RET-MB was exposed to limited air, and then the tubes were stored in an oven in vertical position. After the preselected storage duration of 1, 3, 7, and 14 days, the tubes were removed from the oven, and the properties of the RET-MBs were analyzed. All the fresh and stored RET-MBs exhibited phase stability, as determined through ASTM D7173 [14, 21].

Stability of the base binder during storage

As the RET-MBs are studied for property erosion due to high-temperature storage, it is imperative to ask whether the changes within the pristine binders contribute to the observed property changes. To check any property variation in the base binders during high-temperature storage, binder B₁ was stored in the oven for 1, 3, 7, and 14 days at 150°C temperature. Figure 2 shows the variation of softening point and penetration values as a function of storage days, where the binder exhibits only negligible change during storage. FTIR plots of the fresh and seven-day stored binder are shown in the inset of Fig. 2. Fresh and stored binders display no difference, which clearly indicates that the selected binder remains stable under the storage conditions used in this study. Hence, any property erosion in RET-MB during storage can be mainly attributed to the RET and PPA system.

3. Results and Discussion

3.1 Effect of storage temperature and time

Studies have shown that storage temperature and time play an essential role in the property deterioration in styrene-butadiene-styrene modified binders [21, 23]. This study evaluates the effect of storage temperature and time on the properties of the RET polymer modified binder. A comprehensive study was carried out on ‘RET₁-MB₁’ with 2 wt.% RET₁ polymer and 0.2 wt.% PPA in B₁ binder (B₁-2%RET₁-0.2%PPA). Considering the practical storage and transportation scenarios, the RET₁-MB₁ modified binder was stored in sealed aluminum tubes at 120, 135, 150, and 165°C for up to 14 days. Generally, if the RET-MBs are anticipated to be used after a week for pavement construction, they are stored at temperatures below 150°C to save on energy costs. Hence, the effect of storage on the conventional and rheological properties of RET₁-MB₁ was assessed at 120 and 135°C.

The softening point value of asphalt binders gives a general indication of the binders load-carrying capacity at upper service temperatures. Generally, the higher the softening point value, the better is the binder’s resistance to rutting at upper service temperatures. Figure 3 shows the changes in the softening point value of the RET₁-MB₁ as a function of storage temperature and time. At the storage temperature of 120°C, the decrease in softening point was insignificant (≈ 1.2°C) even after 14 days of storage. At the storage temperature of 135°C, the reduction of ≈ 2.2°C can also be considered marginal. However, a significant decrease in softening point
value occurs as the storage temperature is increased to 150°C, ≈ 4 and 6°C after 7 and 14 days of storage. The rate of deterioration rises further when the storage temperature is increased to 165°C. The softening point decreases by ≈ 6 and 8°C after 7 and 14 days of storage at 165°C. Such a magnitude of property erosion during storage at temperatures ≥ 150°C in the limited presence of air is surprising and may result in the modified binder failing the intended specification.

Similar to the softening point parameter, the PG upper limiting temperature ($T_u$) corresponds to the binder’s resistance to rutting. $T_u$ indicates the maximum pavement design temperature at which the parameter $|G^*|/\sin\delta \geq 1$ kPa for unaged binders. As per the ‘Strategic Highway Research Program (SHRP),’ the limiting value of $|G^*|/\sin\delta$ parameter at the pavement design temperature reduces rutting by preventing tenderness in the unaged asphalt binders [34]. The change in $T_u$ value of the RET$_1$-MB$_1$ as a function of storage temperature and time is shown in Fig. 4 (a). Similar to the softening point value deterioration, $T_u$ also decreases significantly at storage temperatures > 150°C. At 120°C storage temperature, the decrease in $T_u$ was insignificant (≈ 1°C) after 14 days. At 135°C storage temperature, the extent of reduction in $T_u$ becomes noticeable ≈ 3°C after 14 days. At 150°C, the $T_u$ value decreases ≈ 3.7°C (from 73.5°C to 69.8°C) within 7 days of storage, which means that the RET$_1$-MB$_1$ fails to meet the PG-70 grade criterion. At 165°C, one grade drop occurs within 3 days of storage. Using such RET-MBs with decreased PG grade may result in the premature failure of asphalt pavements.

Along with load-bearing capacity indicated by softening point and $T_u$ values, good elastic recovery is desirable in modified binders to avoid permanent deformation. When a vehicle passes over the asphalt pavement, the pavement should have the ability to ‘give,’ and at the same time must recover back to its original shape [35]. The % elastic recovery (%ER) values for RET$_1$-MB$_1$ are plotted as a function of storage temperature and time in Fig. 4 (b). Similar to softening point and $T_u$ parameters, the %ER also shows deterioration as a function of storage temperature and time. Ironically, the %ER of the RET$_1$-MB$_1$ decreases from 80% to ≈ 70%, 60%, 30%, and 20% after storage for 7 days at 120, 135, 150, and 165°C, respectively. The %ER decreases further with the increase in storage time to 14 days. The decrease in the elastic nature indicates damage to the binder’s stress-dissipating ability, which may result in poor performance of asphalt pavements.

To further understand the effect of storage temperature and time on the rheological properties of the RET$_1$-MB$_1$, frequency sweep measurements were carried out at 60°C in the linear viscoelastic (LVE) region. Figure 5 presents the complex viscosity ($\eta^*$) and phase angle ($\delta$) values at 60°C as a function of angular frequency (\omega) for the RET$_1$-MB$_1$ stored at 150°C. Figure 5 clearly shows the decrease in complex viscosity of the modified binder due to storage at 150°C. Phase angle ($\delta$) is considered a sensitive parameter representing the state of the polymer network present in the modified binders. It is evident from the inset of Fig. 5 that as the storage duration increases, the phase angle value increases, indicating that the binder will have a reduced elastic response. The divergence among the samples as a function of storage time is more evident at lower frequencies due to the sluggish movements of the RET polymer molecules in the binder [36–38].

### 3.2 Effect of base binder and polymer type

**Base binder type**
To assess the role of the base binder on the extent of property erosion during storage at elevated temperatures, RET-MB was prepared in base binder ‘B_2’ (B_2-2% RET_1-0.2%PPA) and stored at 120, 135, 150, and 165°C. A harder-grade binder (B_2) was selected to prepare RET-MB to determine if a stiffer-grade binder results in a noticeable deviation in the behavior during high-temperature storage. The properties of fresh base binder B_2 and RET_1-MB_2 modified binder (B_2-2%RET_1-0.2%PPA) are given in Table 1. It can be observed in Table 1 that the stiffer base binder ‘B_2’ resulted in a modified binder with improved high-temperature stiffness and elastic recovery properties. Compared to RET_1-MB_1, the softening point, T_u, and %ER values of fresh RET_1-MB_2 were higher by ≈ 10°C, 20°C, and 20%, respectively.

The property changes in the RET_1-MB_2 modified binder as a function of storage temperature and time are presented in Table 2. Similar to the behavior in binder B_1, it can be observed in Table 2 that deterioration in the properties of the RET_1-MB_2 modified binder also occurs due to storage at elevated temperatures. The drop in softening point, T_u, and %ER after 7 days of storage at 150°C was ≈ 5°C, 3.5°C, and 13%, respectively. Owing to the stiffer binder B_2, the decline in properties of RET_1-MB_2 at storage temperatures ≤ 150°C was less severe than in relatively softer grade ‘B_1’ based RET_1-MB_1. However, the property erosion increases significantly at 165°C storage. The drop in softening point, T_u, and %ER after 7 days of storage at 165°C was ≈ 12°C, 10.5°C, and 30%, respectively. The advantage of a stiffer binder was not evident during storage at 165°C. At 165°C, only the drop in %ER values was lower in the case of RET_1-MB_2 compared to RET_1-MB_1.

The observed results reveal that though the base binder affects the property deterioration during storage, a drastically divergent behavior is not observed among the binders. To further illustrate the effect of the base binder, frequency sweep measurements were carried out at 80°C in the LVE region. As B_2 is a stiffer binder, the measurement temperature of 80°C is selected to get a better resolution of property variation during storage. Figure 6 presents the complex viscosity (\(\eta^*\)) and phase angle (\(\delta\)) (plotted in the inset) at 80°C versus angular frequency for the RET_1-MB_2 modified binder stored at 150°C. It can be observed in Fig. 6 that there is a decrease in complex viscosity and an increase in phase angle values during storage at 150°C. Hence, the stiffer binder (B_2) based RET_1-MB_2 modified binder also shows significant deterioration in the rheological properties at storage temperatures ≥ 150°C.
Table 2
Properties of RET$_1$-MB$_2$ and RET$_2$-MB$_1$ binder as a function of storage temperature and time

<table>
<thead>
<tr>
<th>Storage Parameters</th>
<th>Binder Type (B$_2$)</th>
<th>Polymer Type (RET$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RET$_1$-MB$_2$</td>
<td>RET$_2$-MB$_1$</td>
</tr>
<tr>
<td>Storage Temp. (°C)</td>
<td>Storage Duration (Days)</td>
<td>SP (°C)</td>
</tr>
<tr>
<td>Fresh</td>
<td>0</td>
<td>79.0</td>
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<tr>
<td>120</td>
<td>1</td>
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</tbody>
</table>

Polymer type

To understand how a terpolymer of E-nBA-GMA and E-E-GMA type with different compositions affects the properties of the RET-MB during high-temperature storage, another commercial-grade reactive terpolymer ‘RET$_2$’ was utilized for preparing the modified binder in B$_1$. RET$_1$ and RET$_2$ terpolymers have similar ethylene and GMA blocks but have different 3rd repeating monomeric block (n-butyl acrylate vs. vinyl acetate). The properties of the polymer RET$_2$ and the modified binder ‘RET$_2$-MB$_1$’ are given in Table 1. The properties (softening point, T$_u$, and %ER) of fresh and stored RET$_2$-MB$_1$ are given in Table 2. It can be observed in Table 2
that compared to RET$_1$-MB$_1$, the softening point, $T_u$, and %ER values of fresh RET$_2$-MB$_1$ were lower by $\approx 2^\circ$C, 4$^\circ$C, and 25%, respectively.

Similar to RET$_1$-MB$_1$, the properties (softening point, $T_u$, and %ER) of RET$_2$-MB$_1$ also deteriorate during storage. The drop in softening point, $T_u$, and %ER after 7 days of storage at 150$^\circ$C was $\approx 6^\circ$C, 3.4$^\circ$C, and 20%, respectively. Similarly, the drop in softening point, $T_u$, and %ER after 7 days of storage at 165$^\circ$C was $\approx 9^\circ$C, 4.3$^\circ$C, and 37%, respectively. Figure 7 presents the complex viscosity ($\eta^*$) and phase angle ($\delta$) (inset) at 60$^\circ$C versus angular frequency for 150$^\circ$C stored binder. The complex viscosity decreases with storage duration while the corresponding phase angle increases, reinforcing the finding of increased temperature susceptibility and reduced elastic response in the RET-MBs due to elevated temperature storage.

### 3.3 Effect of PPA content

The results presented in sections 3.1 and 3.2 clearly indicate that significant property deterioration in RET-MB is observed at storage temperatures $\geq 150^\circ$C irrespective of the type of base binder and RET polymer. Further, the vital role of PPA content was explored, which provided essential hints about the reason for the severe property deterioration in RET-MB during storage. RET-MBs were prepared by adding 2 wt.% of RET$_1$ polymer in binder $B_1$, and varying the PPA content by 0, 0.1, 0.2, and 0.3 wt.%.

Table 3 presents the properties of the modified binder before and after storing the samples at 150$^\circ$C. It can be observed in Table 3 that increasing the PPA content from 0 to 0.3 wt.% increases the softening point, $T_u$, %ER, and viscosity at 60$^\circ$C of fresh RET$_1$-MB$_1$ by $\approx 9^\circ$C, 9.4$^\circ$C, 60%, and 1100 Pa.s, respectively. The property enhancement may be due to one or the synergy of the following reasons: PPA enhanced base binder stiffness, enhanced the intramolecular interaction between the polymer molecules, enhanced the interaction within the RET – binder system, and enhanced the swelling of the RET molecules [5, 6, 12, 13].

In contrast to the observations made in previous sections, the properties of RET$_1$-MB$_1$ without PPA increase during the first 3 days at 150$^\circ$C and eventually exhibit gelation. Interestingly, the gelled sample is completely soluble in toluene, which indicates that the gelation was caused by secondary interactions. If the gelation was due to covalent crosslinking, the sample would have been insoluble in toluene. In line with the observations made in previous sections, the properties of the RET-MBs with 0.1, 0.2, and 0.3 wt.% PPA content decreases due to storage at 150$^\circ$C.

After 7 days of storage at 150$^\circ$C, the softening point of the RET$_1$-MB$_1$ with 0.1, 0.2, and 0.3 wt.% PPA reduces by $\approx 4.6$, 4.4, and 5.4$^\circ$C, respectively. Similarly, $T_u$ of the modified binders with 0.1, 0.2, and 0.3 wt.% PPA drops by $\approx 2.6$, 3.5, and 2.8$^\circ$C, respectively. %ER and viscosity at 60$^\circ$C also shows significant drop after storage at 150$^\circ$C. The results clearly show that PPA drastically affects the behavior of fresh and stored RET-MBs. To understand the reason behind the property deterioration in RET-MB during storage, a comprehensive study involving FTIR, GPC, and solvent extraction methods was carried out, and the results are presented in the subsequent section.
### Table 3
**RET$_1$-MB$_1$ properties as a function of PPA content and at 150°C storage**

<table>
<thead>
<tr>
<th>PPA Content (%)</th>
<th>Storage Duration (Days)</th>
<th>SP (°C)</th>
<th>$T_u$ (°C)</th>
<th>ER @ 60°C (%)</th>
<th>Vis. @ 60°C (Pa.s)</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>63.4</td>
<td>65.2</td>
<td>28</td>
<td>324</td>
</tr>
<tr>
<td>1</td>
<td>64.4</td>
<td>65.5</td>
<td>42</td>
<td>373</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>68.2</td>
<td>68.5</td>
<td>58</td>
<td>623</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Gel (But soluble in toluene)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>0</td>
<td>65.8</td>
<td>71.5</td>
<td>62</td>
<td>883</td>
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<tr>
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<td>63.0</td>
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<td>57</td>
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<tr>
<td>3</td>
<td>62.2</td>
<td>69.4</td>
<td>52</td>
<td>683</td>
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</tr>
<tr>
<td>7</td>
<td>61.2</td>
<td>68.9</td>
<td>42</td>
<td>652</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>60.2</td>
<td>67.7</td>
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<tr>
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<td>67</td>
<td>809</td>
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<td>756</td>
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<td>70.0</td>
<td>34</td>
<td>559</td>
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</tr>
<tr>
<td>14</td>
<td>61.8</td>
<td>69.0</td>
<td>22</td>
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<tr>
<td>0.3</td>
<td>0</td>
<td>72.2</td>
<td>74.6</td>
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<td>1430</td>
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<tr>
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<tr>
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<td>63.4</td>
<td>70.5</td>
<td>48</td>
<td>727</td>
<td></td>
</tr>
</tbody>
</table>

### 3.4 FTIR, GPC, and solvent extraction methodology:

**Analysis of base binder and RET-MB**

To determine the reason for the severe deterioration in the properties of RET-MB, fresh and stored RET$_1$-MB$_1$ (B$_1$-2% RET$_1$-0.2%PPA) were analyzed using FTIR and GPC techniques. It can be seen in Fig. 8 that since the RET polymer content is only 2 wt.%, the peaks originating from the base binder B$_1$ dominate the FTIR spectra in fresh RET$_1$-MB$_1$. Specifically, epoxy group interaction with the binder is unclear since the region (1200 – 800
containing the epoxy peaks is dominated by binder peaks. Only the peak at 1732 cm$^{-1}$ associated with the carbonyl group in the ester functionality of RET polymer shows up. The peak at 1732 cm$^{-1}$ in RET$_1$-MB$_1$ demonstrates that the carbonyl group of RET polymer does not react/interact with the binder or the PPA.

Similarly, the FTIR spectra of fresh and stored RET$_1$-MB$_1$ samples also show no visible changes, implying that no significant changes occur in the base binder and carbonyl group (1732 cm$^{-1}$) of RET polymer during storage. The GPC chromatogram of the fresh and stored RET$_1$-MB$_1$, presented in the inset of Fig. 8, shows two peaks. The peak near the elution time of 22 mins corresponds to asphaltene molecules of the binder B$_1$, while the peak near 26 mins corresponds to maltene molecules [39, 40]. The result illustrates no significant changes in the asphaltene and maltene peaks of fresh and 7 days stored RET$_1$-MB$_1$, illustrating that the base binder composition does not change during storage in closed metal containers.

**Analysis of binder-PPA system**

FTIR and GPC analysis was carried out on the asphalt binder B1, fresh and stored ‘B1 + 0.2% PPA’ sample to understand the changes in the interaction between the binder and PPA molecules. As shown in Fig. 9, the FTIR spectra and GPC chromatogram of the three samples display no discernible changes. The result indicates that only secondary interactions occur between the base binder and PPA molecules, and the ‘B1 + 0.2% PPA’ sample remains stable during storage at 150°C. Also, the result suggests that the deterioration in RET-MB properties during storage may be due to the changes in the interaction between the RET polymer and PPA molecules.

**Analysis of RET$_1$-PPA system**

Next, the changes in the interactions between RET$_1$ and PPA were analyzed using the FTIR technique. Films of RET$_1$ polymer, with and without PPA, were prepared using toluene. The RET$_1$ polymer was first dissolved in toluene at 75°C, and 0.2 wt.% of PPA was added to the solution. The films were obtained by completely evaporating the toluene solvent. The films were then sealed in petri dishes and stored in an oven for 1 day at 150°C. The FTIR analysis of the films, before and after storage, are presented in Fig. 10. FTIR spectra of fresh and 1 day-150°C stored RET polymer without PPA were similar, which implies that the RET polymer without PPA was stable after storage at 150°C for 1 day.

However, the RET$_1$ sample with 0.2 wt.% PPA shows significant changes in FTIR spectra after 1 day of storage. From Fig. 10, it's apparent that the epoxy peak of GMA near 910 cm$^{-1}$ disappears entirely after 1 day of storage, which means the epoxy ring interacts with the PPA molecule [30, 41, 42]. Additionally, the spectra between 1040 and 1010 cm$^{-1}$ broaden significantly due to the formation of phosphate ester linkage [43, 44]. Hence, the epoxy ring in the RET polymer strongly interacts with PPA molecules to form a phosphate ester moiety during storage. Due to the interaction of the highly polar epoxy ring in the RET polymer during storage, its ability to interact with the binder molecules reduces, because of which severe property erosion is observed in RET-MBs during storage at elevated temperatures. The 3 and 7 days stored RET$_1$ films reveal no discernible changes in FTIR analysis; hence, their results are not shown for brevity.

**Solvent extraction study**
The reduction in the interaction within the RET – binder system during storage is supported by the solvent extraction experiments using n-heptane. The asphaltene fractions of the asphalt binder precipitate in n-heptane, and hence, n-heptane treatment of asphalt binder and RET-MB (both fresh and 7 days stored at 150°C) was performed [45]. The n-heptane residue, which is mostly the asphaltene fraction, is studied for interactions between the RET and asphaltene fraction of the binder and the changes in the interactions as a result of elevated temperature storage of RET-MB [7].

100 g of asphalt binder B₁ was mixed with 1000 ml of n-heptane using a low-shear mixer for 90 minutes at 75°C, and the solution was kept overnight undisturbed in a closed beaker. As shown in Fig. 11, ≈ 10 wt.% brittle powder residue was obtained after filtering the solution and drying. Next, 100 g each of fresh and stored RET₁-MB₁ samples were mixed in 1000 ml of n-heptane. Unlike the case of base binder B₁, lumps of residue were obtained after 90 minutes of stirring at 75°C, as shown in Fig. 11. After filtering, ≈ 25 wt.% and 15 wt.% of lumpy samples were obtained from fresh and stored RET₁-MB₁.

The ≈ 25 wt.% residue from the fresh RET₁-MB₁ consisted of a few large rubbery lumps. Compared to the residue from the base binder, the increase in the wt.% of the residue from the fresh RET₁-MB₁ indicates good interaction between the RET polymer and binder molecules, which results in a higher n-heptane insoluble fraction. In comparison, the decreased (≈ 15 wt.%) residue from 7 days 150°C stored RET₁-MB₁ was composed of lumps of smaller size and with a depleted rubbery nature, illustrating lower RET polymer.

The FTIR spectra of the residues are also presented in Fig. 11. The carbonyl peak at 1732 cm⁻¹ confirms the presence of RET₁ polymer in the residues of fresh and stored RET₁-MB₁. Notably, the intensity of the 1732 cm⁻¹ peak in the stored RET₁-MB₁ residue is lower than the fresh RET₁-MB₁ residue, implying lower polymer content in the residue of the stored RET₁-MB₁. Thus, the FTIR results support the reduced wt.% and rubbery consistency of the residue from the stored RET₁-MB₁. The loss of polymer from the residue of stored RET₁-MB₁ clearly illustrates a depleted interaction between the RET₁ polymer and binder molecules during elevated temperature storage.

Conclusions

The effect of storage time and temperature on the properties of RET modified binders (RET-MBs) was evaluated in this study. Literature studies have shown significant depletion in the properties of SBS modified binders (SBS-MBs) during storage at temperatures ≥ 180°C. Our results show that the extent of property deterioration in RET-MBs is more severe than in SBS-MBs. The following important conclusions can be summarized.

• Storage temperature and time:

The storage temperature profoundly influences property erosion in RET-MBs, even in sealed containers. For the RET₁-MB₁, even at a low storage temperature of 120°C, the % elastic recovery (%ER) values decrease by 10% after 14 days of storage. Increasing the storage temperature to 135°C, the $T_u$ and %ER values decrease by 3°C and 40% after 14 days of storage. A similar magnitude of drop can be observed in $T_u$ within the first three days.
of storage at 150 and 165°C. The %ER value drops from 80% to ≈ 30% and 20% after only 7 days of storage at 150 and 165°C, respectively.

• Base binder, RET polymer, and PPA concentration:

The properties of fresh RET-MB were higher in stiffer binder B₂. However, except for lower erosion in %ER values, no major benefit of a stiffer binder was observed during storage at 165°C. The observed results reveal that though the base binder affects the property deterioration during storage, a drastically divergent behavior was not observed.

Property erosion was observed even in a different RET polymer of EEGMA type but with a different composition. The initial properties of the RET-MB in the alternate polymer were much lower, due to which the extent of deterioration was lower. Increasing the PPA dosage enhances the properties of fresh RET-modified binders. However, no clear benefit is observed in the extent of erosion in various properties as a function of PPA concentration.

• FTIR and GPC analysis:

**RET modified binder**

Owing to only 2 wt.% of RET content, the peaks originating from the base binder dominate the FTIR spectra in fresh RET-MB. Hence, changes in the interaction within the RET – binder system during storage were not discernable. The FTIR spectra of fresh and stored RET-MB samples show no visible changes, implying that no significant changes occur during storage in the base binder and carbonyl group of RET polymer. GPC results also illustrate that the base binder composition does not change during storage in closed metal containers.

**Binder + PPA**

FTIR and GPC analysis indicates only secondary interactions between the base binder and PPA molecules. Storage does not result in major changes in the binder + PPA system.

**RET + PPA**

The FTIR spectra of fresh and 1 day-150°C stored RET polymer without PPA were similar, which implies that the RET polymer without PPA was stable after storage at 150°C for 1 day. On the contrary, FTIR spectra of RET polymer with PPA indicate a strong interaction of the epoxy ring with the PPA molecules to form phosphate ester during storage. Due to this interaction, the ability of the RET polymer to interact with the binder molecules reduces, because of which severe property erosion is observed in RET-MBs during storage at elevated temperatures. The reduction in the wt.% of n-heptane extracted residue for the stored RET-MB also indicates the reduction in the interaction between RET and binder molecules.

• Storage recommendation for RET-MB: Since PMBs are generally stored and transported at higher temperatures and storage and handling guidelines issued by various agencies, but no specific guidelines are currently available for RET-MBs. From this study, we recommend that RET-MBs should not be stored and transported at temperatures >135°C.
Declarations

Declaration of Conflict of Interest

The authors declare that they have no competing financial interests or personal relationships that could have appeared to influence the work reported in this research.

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Figure 1

Chemical structure and FTIR spectra of RET₁ polymer between 2000-600 cm⁻¹
Figure 2

Softening point and penetration values @ 25 °C for the binder $B_1$ as a function of storage days at 150 °C. Inset shows FTIR plots of the fresh and 7 days-150 °C stored binder $B_1$. 
Figure 3

Softening point vs. storage duration at different temperatures for RET₁-MB₁ binder
Figure 4

(a) PG upper limiting temperature ($T_u$) and (b) Elastic recovery (%ER) at 60 °C vs. storage duration at different temperatures for RET$_1$-MB$_1$ binder
Figure 5

Complex viscosity ($\eta^*$) vs. angular frequency ($\omega$) at 60 °C for RET$_1$-MB$_1$ modified binder stored at 150 °C. The inset shows the phase angle ($\delta$) vs.
Figure 6

Complex viscosity ($\eta^*$) vs. angular frequency ($\omega$) at 80 °C for RET$_1$-MB$_2$ modified binder stored at 150 °C. Inset presents the phase angle ($\delta$) vs.
Figure 7

Complex viscosity ($\eta^*$) vs. angular frequency ($\omega$) at 60 °C for RET$_2$-MB$_1$ modified binder stored at 150 °C. Inset presents the phase angle ($\delta$) vs.
Figure 8

FTIR and GPC results of fresh base binder $B_1$, fresh and 7 days-150 °C stored $RET_{1-MB_1}$
Figure 9

FTIR spectra of fresh base binder B₁, fresh and 7 days-150 °C stored 'B₁+0.2% PPA' The inset shows the GPC results of the three samples
Figure 10

FTIR spectra of fresh and 1 day-150 °C stored RET$_1$ polymer with and without PPA
Figure 11

Physical appearance and wt.% of residue from n-heptane of base binder $B_1$, fresh and $7$ days-150 °C stored $\text{RET}_1$-$\text{MB}_1$, and FTIR spectra of the three residues.