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Assessment of antioxidant resistance to thermal - oxidative degradation of stabilized polybutadiene binder

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Abstract. polybutadiene is the most common polymeric binder for composite solid propellants. This polymer suffers from oxidative degradation reactions on storing with deterioration in mechanical properties. Certain anti-oxidant materials can retard such reaction offering enhanced aging characteristics. In this study, two different primary antioxidants including phenol-based (AO2246) and amine-based (Flexzone 6H) were employed to stabilize polybutadiene polymer. Oxidation induction time (OIT) was evaluated using isothermal DSC. High OIT value means high resistance to oxidative degradation. The impact of anti-oxidant on mechanical properties was evaluated using shore A. Flexzone 6H significantly improved binder oxidative stability with an increase in OIT value by 20 folds with significant decrease in oxidation enthalpy. Flexzone 6H can offer enhanced resistance toward oxidative reactions; as it can act as efficient H atom donor to break down chain degradation reaction. Additionally, the three stabilized aromatic rings can capture free radicals. AO2246 enhanced the binder mechanical characteristics during aging at 80 °C using Shore A test. In the meantime, AO2246 could enhance the mechanical properties due to its integration into the polymeric matrix due to –OH functional groups. The two antioxidants demonstrated controversy effects. Whereas Flexzone 6H offered enhanced resistance to oxidative degradation; AO2246 offered enhanced mechanical properties.

1. Introduction

Composite propellant is a heterogeneous mixture composed mainly of inorganic oxidizer, metallic fuel, and polymeric binder. Polymeric binder is the main ingredient responsible for holding all ingredients together and rendering the required mechanical properties to the polymeric matrix. Hydroxy terminated polybutadiene (HTPB) is the most common polymer in use for composite solid propellants. HTPB has several advantages including: low glass transition temperature, high tensile strength, good chemical resistance, high compatibility with propellant solid ingredients [1, 2]. HTPB has high ability to accommodate solid loading up to 88 %. Additionally, HTPB can act as fuel producing large volume of gaseous products. HTPB is the backbone of polymeric matrix; it constitutes about 93 % of polymeric binder [3, 4]. High mechanical properties are mandatory for safe storing, transportation, and firing. During firing the propellant grain will be exposed to severe thermal and pressure stresses [5, 6].

HTPB can offer high degree of un-saturation that is required to provide the composite propellant with its viscoelastic nature and flexibility. On the other hand, these un-saturated bonds are very sensitive to oxidation [7, 8]. Various slow chemical oxidative reactions (aging reactions) can take



place on storing. These oxidative reactions include peroxidation, hydro-peroxidation, cross linking by peroxide linkage figure 1; further details can be found in the following reference [9].

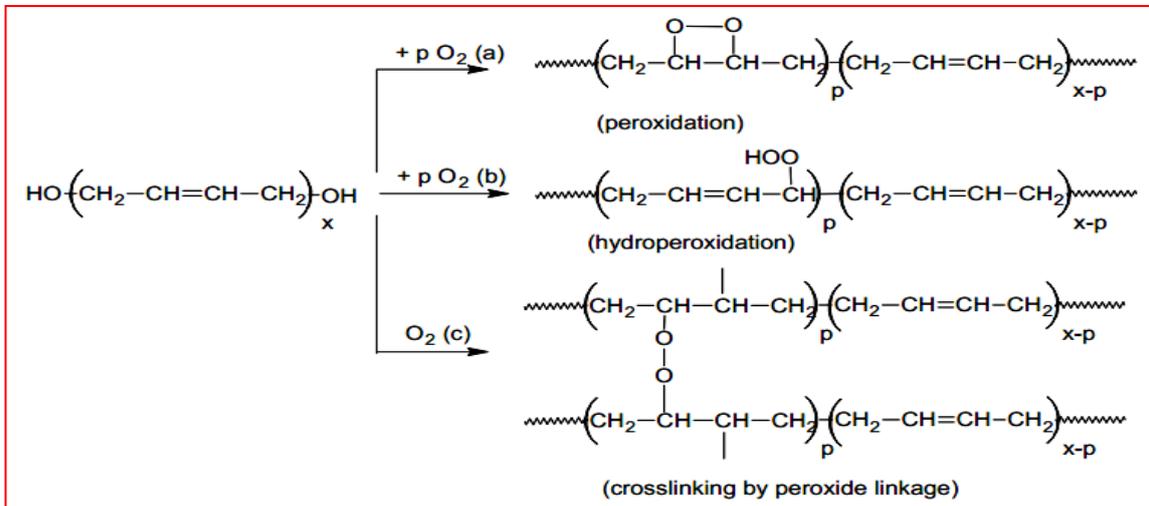


Figure 1. Thermal oxidative degradation reactions of HTPB prepolymer.

As the binder is exposed to thermal loading during processing and storage, free radicals (R^\cdot) are formed. Such radicals can react with oxygen forming peroxy radicals (ROO^\cdot). These radicals further react with labile hydrogen atoms of the binder to form unstable hydroperoxides (ROOH) which immediately decompose via hemolytic cleavage to form alkoxy and hydroxyl radicals figure 2.

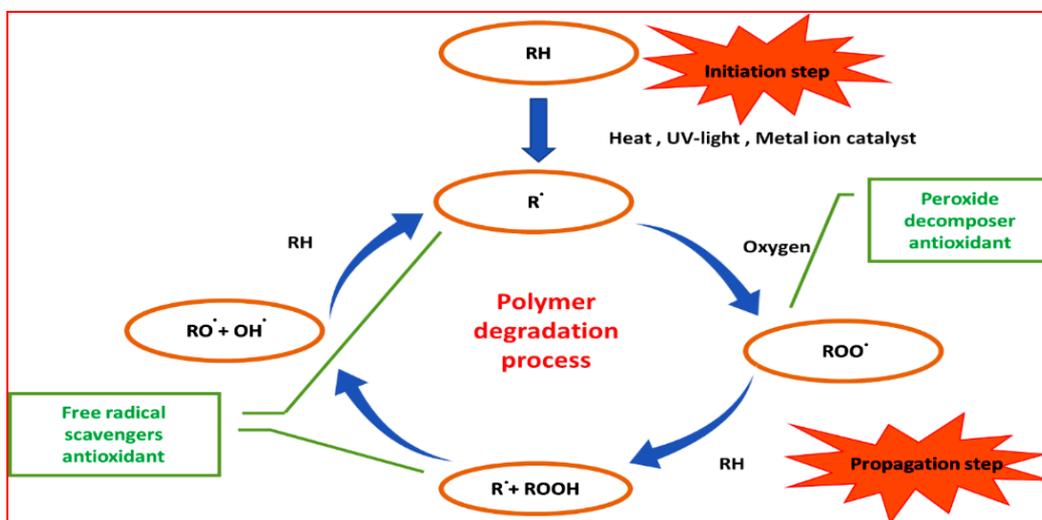


Figure 2. General scheme of thermal-oxidative degradation of polymer

These oxidative reactions have unfavorable effect on the characteristic viscoelastic nature of the composite propellants and could result in deterioration of propellant mechanical properties by propagating through the whole propellant grain and causing integral system failure. Antioxidant materials can stabilize the binder against these oxidative reactions [10, 11]. Generally, antioxidants can be classified into two main classes including:

- Primary antioxidants: these antioxidants break the degradation chain by donating H- atoms to free radicals. Therefore, it could prevent those radicals from propagating the chain reaction. The chemical structure of such anti-oxidant includes pendant phenols or aromatic amines.
- Secondary antioxidants: these antioxidants can act as hydroperoxide decomposers like phosphites and thioester [12, 13].

Primary antioxidant is the most common for composite propellant as it suppresses the oxidative reactions from the start point. Antioxidant depletion is strongly related to an oxidative crosslinking process as once the antioxidant is depleted, thermal oxidative degradation will proceed rapidly [12]. Such a complex oxidative crosslinking reaction could be investigated by monitoring the increase of mass variation as a result of oxygen uptake, double bond disappearance, carbonyl build-up, and change of mechanical property (hardening) as a result of further crosslinking [13]. Kinetic parameters such as activation energy could be considered as the key parameter for service life assessment of composite propellant by analysis of the provided data about binder thermal-oxidative degradation [14, 15].

2. Experimental

2.1. Chemicals and materials

The employed polymer was hydroxyl terminated polybutadiene (HTPB) with 0.8495 mg. eqv. OH/g (Aldrich). Curing agent was hexamethylene diisocyanate (HMDI) with 11.86 mg. eqv. NCO/g (Aldrich). Different anti-oxidants including 2,2'-methylene bis 6-t-butyl-4-methylphenol (AO 2246) and N, N'-diphenyl-p-phenylenediamine (Flexzone 6 H) (Alpha Chemica) were employed. The chemical structure of employed anti-oxidants is demonstrated in figure 3. All chemicals were used as received without further treatment

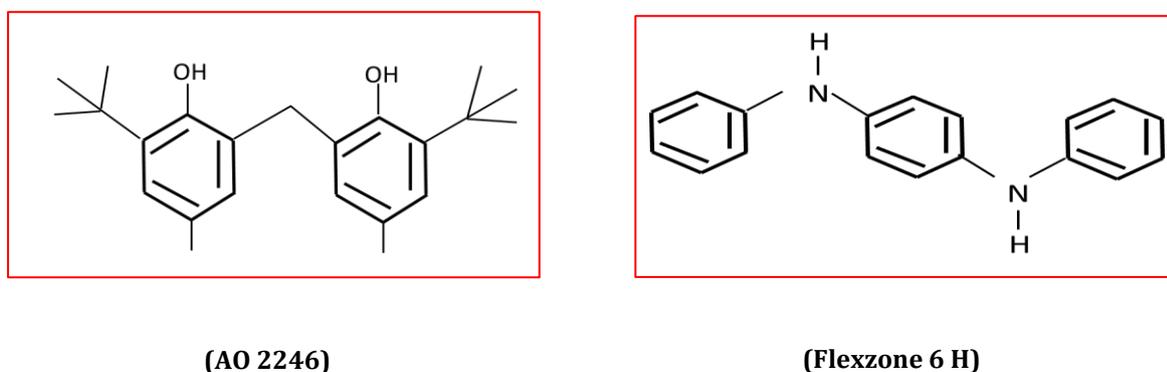


Figure 3. Chemical structure of antioxidants: AO-2246, and Flexzone 6H.

2.2. Binder stabilization

Poly-butadiene polymer was mixed with representative amount (2 wt %) of different anti-oxidants. The mixing process was conducted in a vertical mixer; the employed mixing speed was 30 rpm. The mixing temperature was 45 °C, controlled with hot circulated water. Cross linking agent (HMDI) was introduced by the end of mixing process. Consequently, the cross-linked binder was cast and cured at 40 °C, under vacuum for 7 days. The employed curing ratio (NCO/OH) was 0.7.

2.3. Impact of anti-oxidant on thermal behaviour

TGA measurement can provide valuable information about degradation temperature, degradation rate, and total weight loss. The impact of anti-oxidant on thermal decomposition was evaluated by

thermal gravimetric analysis TGA, Q500, TA instruments, USA. The tested samples were heated from 25 to 500 °C at 5 °C/min, under N₂ flow of 30 mL/min. DSC measurement can provide valuable data on initial oxidation temperature (T_i), onset oxidation temperature (OOT), oxidation peak temperature (OP), final oxidation temperature (T_f), as well as oxidation enthalpy (ΔH).

Anti-oxidant efficiency for oxidative degradation was evaluated via precise measurement of oxidation induction time (OIT). High OIT value means high resistance to oxidative degradation. This key parameter was evaluated using an isothermal DSC, Q1000 TA Instrument, USA according to the standard method (ASTM D 3895) [16]. The tested sample was placed in an aluminum crucible and heated to 180 °C at 5 °C/min, under N₂ flow of 50 ml/min. The temperature was hold at 180 °C for 5 min. Consequently, the flowing gas was switched from nitrogen to pure oxygen gas. The time interval between flowing gas change to oxygen and the onset point of exothermic oxidation peak (catastrophic degradation or oxidation) was recorded as OIT time [17].

2.4. Impact of anti-oxidant on hardness

Hardness is defined as the material resistance to penetration. Hardness measurements can offer an indication about polymer cross linking efficiency. Higher hardness value is associated with higher degree of crosslinking. The impact of different anti-oxidants on HTPB hardness was measured using Shore A Durometer.

3. Results and discussion

3.1. Initial decomposition temperature using TGA

Thermal behavior of reference binder to binder stabilized with different antioxidants was investigated using TGA (Figure 4). It is obvious that the thermal behavior of stabilized binder is similar to non-stabilized binder; no degradation could take place up to 210 °C. It can be assumed binder stabilized with AO2246 is more resistant to degradation as it could be integrated into the polymer chain via bonding with its –OH functional group [18].

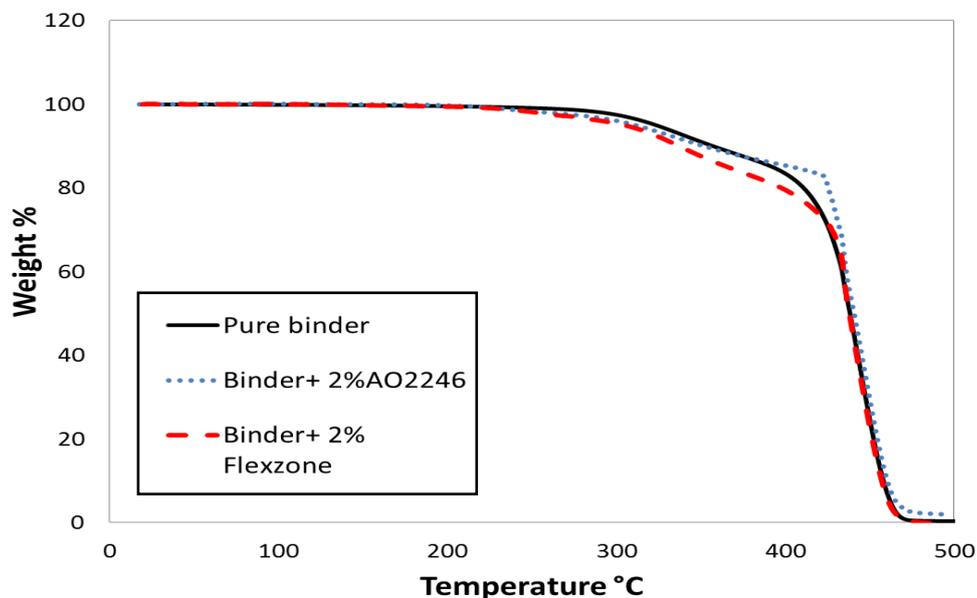


Figure 4. Thermo-gravimetric (TGA) results.

3.2. Thermal behaviour using dynamic DSC

It apparent that thermal decomposition of HTPB take place in two separated stages including: thermal oxidation peak, and exothermic heat involved in cyclization process figure 5 [19, 20].

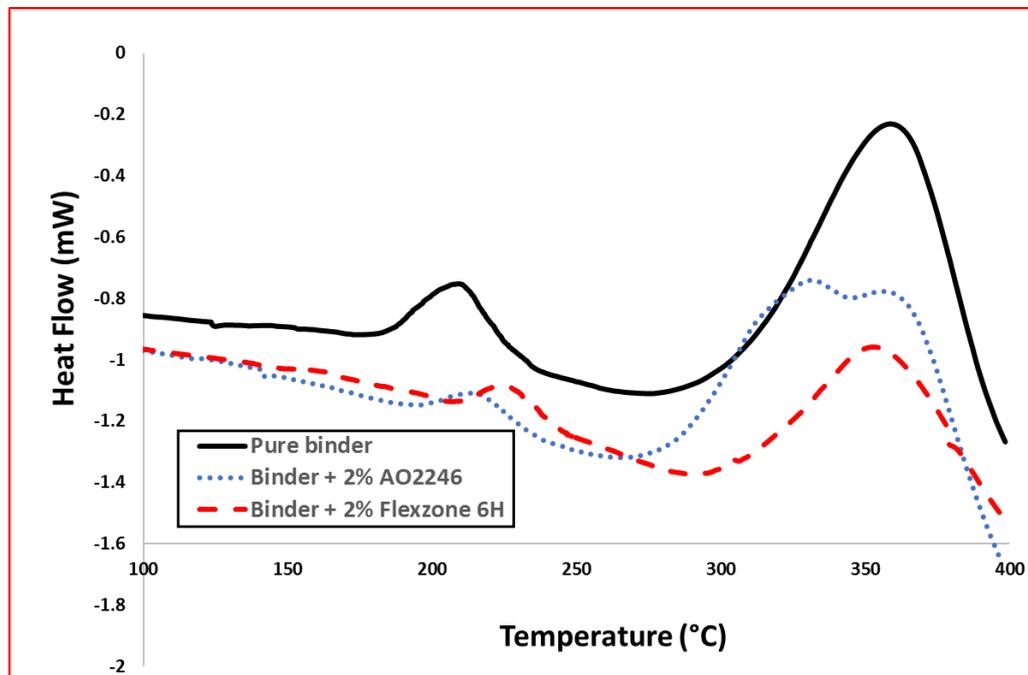


Figure 5. Dynamic DSC thermogram.

Figure 5 demonstrated that there is a dramatic impact of anti-oxidant on oxidation temperature and oxidation enthalpy. A reduction in oxidation enthalpy (energy) and fractional decomposition (relative oxidation energy) were related to improved stability via reduced oxidation effect [19].

Oxidation onset temperature (OOT), and oxidation peak temperature (OP) was evaluated for stabilized binder to non-stabilized binder. Whereas, AO2246 offered an increase in OP and OOT by 4 °C and 5 °C respectively; Flexzone 6H offered increase in OP, and OOT by 13 °C and 17 °C respectively table .1.

Table 1. Thermal-oxidative critical parameters.

	T_i	T_f	OP	OOT	ΔH_{ox}	α
	(° C)	(° C)	(° C)	(° C)	(J/g)	(-)
Pure binder	177.3	237.2	208.4	190.4	37.2	-
Binder + 2 % AO2246	188.2	233.0	213.5	196.5	18.3	0.49
Binder + 2 % Flexzone 6 H	197.1	242.3	221.7	207.8	16.4	0.44

Keys: T_i and T_f: Initial and final oxidation temperature, OP: Oxidation peak temperature OOT: Oxidation onset temperature, ΔH_{ox}: Oxidation enthalpy (energy) and α: fractional decomposition (ΔH/ΔH⁰).

It is apparent that Flexzone 6 H offered the lowest oxidation enthalpy; this oxidation could take place at higher temperature compared with AO2246 and reference polymer.

3.3. Oxidation induction time (OIT) using isothermal DSC

Oxidation induction time (OIT) is an effective parameter to characterize the isothermal oxidation reaction. It evaluates the efficiency of different stabilizers to evaluate the relative resistance of various polymeric hydrocarbon material to oxidation. Figure 6 demonstrates the impact of anti-oxidants on oxidation induction time (OIT).

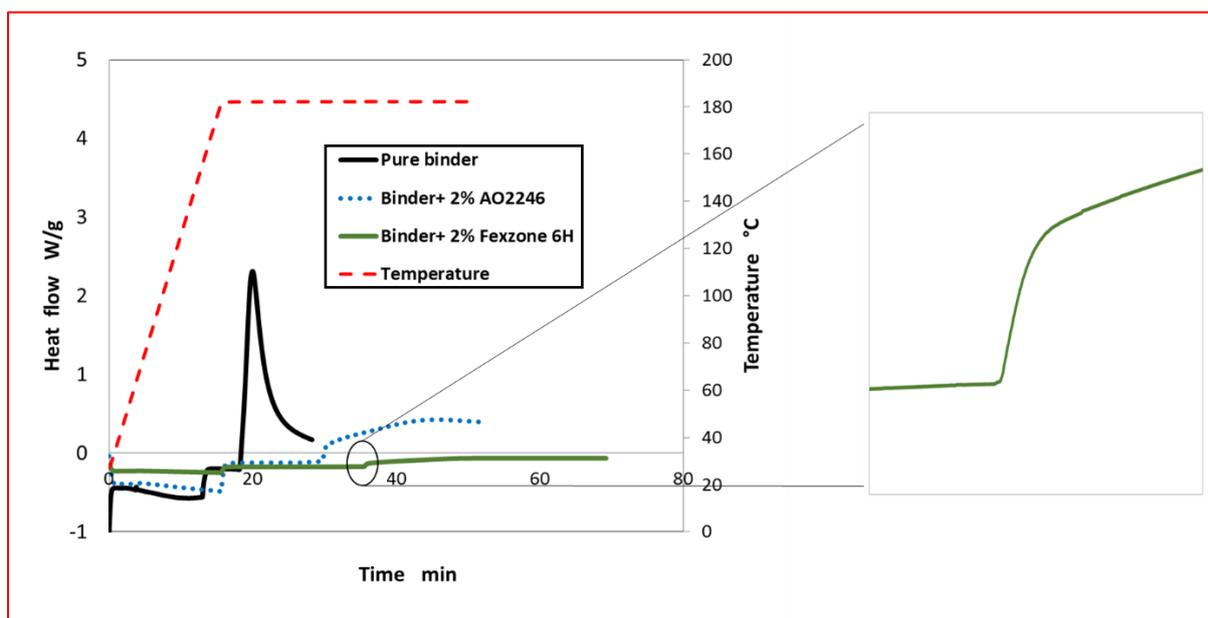


Figure 6. Comparative isothermal DSC thermo-gram.

It is apparent that pure binder has low OIT value of 0.9 min; this means that it is extremely sensitive polymer to oxidation. The two anti-oxidants offered dramatic increase in OIT value. While AO2246 offered an increase in OIT by 13.2 min.; flexzone 6H offered an increase in OIT by 18.9 min table .2. Multifold was defined as the capability to stabilized polymer to resist oxidation with respect to pure binder.

Table 2. OIT values of stabilized and un-stabilized binder

	OIT	Effectiveness
	(min)	(Multi-fold)
Pure binder	0.9	-
Binder + AO2246	13.2	13.7
Binder + Flexzone 6H	18.9	20

Flexzone 6H offered an increase in polymer resistance to oxidation by 20 times. The stabilization mechanism of both AO2246 and Flexzone 6H depend on H atom donor to break down HTPB chain degradation reaction. Whereas stabilization with AO2246 depend on –OH group; the stabilization mechanism of Flexzone 6H depends on –NH group. It can be concluded that part of AO2246 –OH stabilization groups could be involved in cross linking reactions. Therefore less stabilization could

be achieved compared with enhanced mechanical properties due to integration into the polymeric matrix [20 - 24] .

3.4 Hardness monitoring

Hardness testing is a useful method for determination of polymer mechanical changes [25]. Hardness of reference polymer to stabilized polymer was measured; the change of hardness with aging time was further investigated table .3.

Table 3. Hardness variation after aging at 80 °C.

	After curing	After aging (days)		
		12	24	35
Pure binder	68	93	94	95
Binder + 2 % AO2246	42	44	50	58
Binder + 2 % Flexzone 6 H	37	38	43	49

Pure binder demonstrated dramatic increase in hardness with aging time. This gives an indication that it is extremely sensitive polymer to oxidative cross linking. AO2246 offered minimum change in mechanical properties with aging time. This can be ascribed to its integration into the polymeric matrix via OH group [26, 27].

During aging periods visual changes in binder color were observed figure 7. Yellow color is a qualitative indication to investigate the occurrence of oxidative aging reactions. Yellowing could be quantitatively determined by using special spectrophotometer [28].

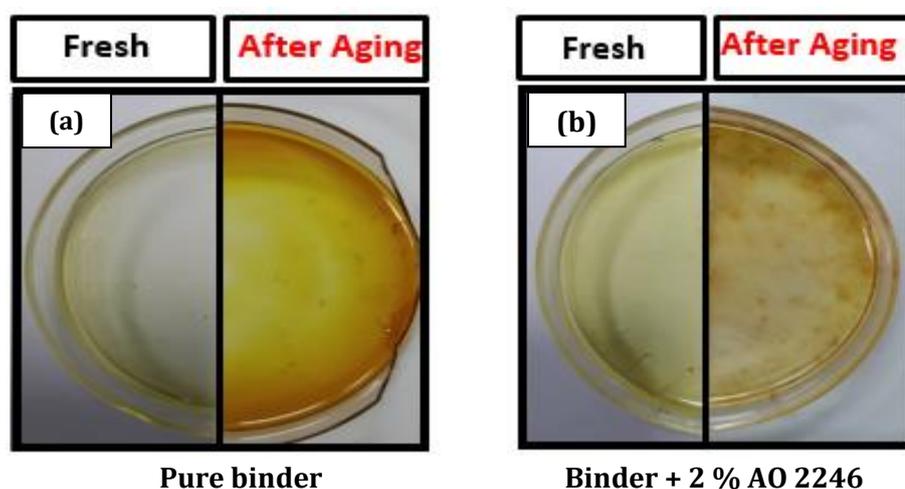


Figure 7. Visual change of non-stabilized and stabilized polymer with 2 percentages of AO2246 antioxidant after curing and after aging at 80 °C for 35 days

Whereas virgin polymer demonstrated dramatic change in color with aging figure 7-a; polymer stabilized with AO2246 demonstrated slight change in yellow color figure 7-b. On the other hand, this test couldn't be performed for Flexzone 6H as it has a dark base color.

4. Conclusions

Antioxidant plays a vital role to increase the thermal stability of the base polymeric matrix. Flexzone 6H offered significant increase in OIT value and enhanced binder resistance to oxidative degradation by 20 folds. This can be ascribed to the availability of H donor groups to break down the oxidative degradation process. In the meantime, AO2246 was found to have the ability to integrate itself into the polymeric matrix (via –OH groups) offering enhanced mechanical properties with aging. This was verified via hardness measurement. It could minimize the availability of reactive OH – groups for oxidative stabilization. It can be summarized that the two antioxidants have controversy stabilization mechanisms that could complete each other.

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