文章编号: 1006-9941(2007)04-0349-03

扩链和交联剂对 NEPE 推进剂胶片高温力学性能的影响

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摘要: 研究了脂肪族、聚醚类二元醇扩链剂和三元醇交联剂对 NEPE 推进剂胶片的高温力学性能影响。结果表明,脂肪族二元醇扩链剂可提高 NEPE 推进剂胶片的高温力学性能,但会引起硝酸酯增塑剂析出;选择适当种类、含量的聚醚类二元醇可显著提高胶片的高温力学性能;三元醇交联剂使 NEPE 推进剂粘合剂胶片的最大抗拉强度有所提高,最大延伸率降低。

关键词: 固体力学; 扩链剂; 交联剂; NEPE 推进剂; 粘合剂体系; 力学性能

中图分类号: V512; TJ5　　　　**文献标识码:** A

1　引　言

在聚氨酯弹性体领域,有关助剂(如扩链剂和交联剂等)对其形态结构及力学性能的影响已经进行了广泛的研究[1~5]。NEPE 推进剂是以聚氨酯弹性体作为粘合剂基体的复合材料,其力学性能调节又是该类推进剂的关键技术之一,可通过键合剂改善胶片与填料界面的粘接性能,使该类推进剂的常、低温(+20 ℃和 −40 ℃)力学性能基本满足战术导弹发动机装药的总体要求。但应用实践表明,该类推进剂的高温(+50 ℃)力学性能(最大抗拉强度 $\sigma_m = 0.35$ MPa; 最大延伸率 $\varepsilon_m = 32\%$)仍然偏低。由于战术导弹发动机工作压强相对较高、飞行过载较大、使用环境较苛刻,仅靠应用键合剂难以进一步提高其力学性能。因此,本文借鉴扩链和交联剂在相关体系的应用经验[6],研究了不同助剂对该类推进剂胶片的形态结构和高温力学性能的影响。

2　实　验

2.1　主要设备和原材料

INSTRON4500 万能材料试验机。扩链剂和交联剂种类及相关参数见表 1。

2.2　配方设计及实验方法

2.2.1　推进剂胶片配方设计

由于 NEPE 推进剂是一种以聚醚粘合剂为基体,由多种功能组分(NG/BTTN、AP、RDX、Al 粉和燃烧催化剂等)共混形成的复合材料,具有大增塑比(P_l: P_o > 2.5)和相对较高的固含量(~75%),推进剂各组分间相互作用复杂,为研究扩链和交联剂对该类推进剂粘合剂基体的影响,本实验暂时不考虑固体组分对粘合剂体系的作用,设计了由粘合剂体系和增塑剂组成的空白配方。

表 1　扩链剂和交联剂种类及相关参数

Table 1　Parameters of the chain extenders and cross linkers

category	chain extender and cross linker	M_n /g·mol^{-1}	[OH] /mgKOH·g^{-1}
aliphatic diols	乙二醇(EGC)	62	1809.7
	丙二醇(PGC)	76	1476.3
	丁二醇(BGC)	90	1246.7
	己二醇(HGC)	118	950.8
polyether diols	一缩二乙二醇(PEG100)	100	1057.3
	二缩三乙二醇(PEG150)	150	747.2
	聚乙二醇(PEG200)	200	561.0
	聚乙二醇(PEG400)	400	280.5
	聚乙二醇(PEG1000)	1000	112.2
triols	丙三醇(GCR)	92	1827.4
	丁三醇(BTR)	106	1587.7
	三甲醇丙烷(TMP)	134	1254.3

粘合剂基体空白配方的组成含量为 PET/N-100, ~29%, NG/BTTN, ~71%, 扩链、交联剂按配方设计参数外加。扩链剂和交联剂的配方参数如表 2 所示。

2.2.2　实验方法

采用配浆浇铸工艺制备 NEPE 推进剂胶片,按配方设计参数计算扩链剂、交联剂及粘合剂基体各组分含量,混合,真空浇铸,固化。

采用万能材料试验机测试推进剂粘合剂胶片的高温(+50 ℃)力学性能,样品尺寸 2 mm × 4 mm × 10 mm,单轴拉伸速率 2 mm·min^{-1}。

凝胶分数采用索氏提取法进行测定。将推进剂药块切成碎片,准确称取一定量的样品置于索氏提取器

收稿日期: 2007-04-19; **修回日期:** 2007-06-18

基金项目: 总装预研基金(41328030306)

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中,加入溶剂使其充分溶胀。提取可溶物并且除去溶剂,由提取前后样品的重量即可得到凝胶分数。

表 2 含扩链剂和交联剂的配方参数

Table 2 Parameters of the binder films containing the chain extenders and cross linkers

$N_{OH-助}/N_{OH-PET}$ 1)	1/4	3/7	1/2	1/1
samples with chain extender	EGC-1/4	–	EGC-1/2	EGC-1/1
	PGC-1/4	–	PGC-1/2	PGC-1/1
	BGC-1/4	–	BGC-1/2	BGC – 1/1
	HGC-1/4	–	HGC-1/2	HGC-1/1
	PEG100-1/4	–	PEG100-1/2	PEG10-1/1
	PEG150-1/4	–	PEG150-1/2	PEG150-1/1
	–	–	PEG200-1/2	PEG200-1/1
	–	–	PEG400-1/2	PEG400-1/1
	–	–	PEG1000-1/2	PEG1000-1/1
samples with cross linker	–	GCR-3/7	–	GCR-1/1
	–	BTR-3/7	–	BTR-1/1
	–	TMP-3/7	–	TMP-1/1

Note: 1) $N_{OH-助}/N_{OH-PET}$: The mole ratio of the hydroxide groups of the reagents to the binder.

3 结果与讨论

3.1 脂肪族二元醇扩链剂对粘合剂胶片高温力学性能的影响

按配方设计参数及实验方法分别制备了粘合剂空白配方胶片和含脂肪族二元醇扩链剂的粘合剂胶片,并对其高温(+50 ℃)力学性能进行对比,试验结果见表 3。

表 3 脂肪族二元醇扩链剂对粘合剂胶片高温(+50 ℃)力学性能的影响

Table 3 Effects of the aliphatic diols on the mechanical characteristics of the binder film at 50℃

sample	the state and appearance of the cured films	σ_m/MPa	ε_m/%
blank	Viscoelastic film with dry surface	0.22	96.81
EGC-1/4	Viscoelastic film with the increasing amount of nitrate esters exuded from the film as the chain extender increases	0.35	87.64
EGC-1/2		0.38	73.45
EGC-1/1		0.35	81.08
PGC-1/4	Viscoelastic film with the increasing amount of nitrate esters exuded from the film as the chain extender increases	0.26	77.08
PGC-1/2		0.35	76.57
PGC-1/1		0.48	82.08
BGC-1/4	Viscoelastic film with the increasing amount of nitrate esters exuded from the film as the chain extender increases	0.37	99.42
BGC-1/2		0.45	103.42
BGC-1/1		0.38	63.19
HGC-1/4	Viscoelastic film with the increasing amount of nitrate esters exuded from the film as the chain extender increases	0.26	96.27
HGC-1/2		0.26	80.75
HGC-1/1		0.29	81.97

由表 3 可知,EGC、PGC、BGC 和 HGC 四种二元醇扩链剂使 NEPE 推进剂粘合剂胶片的 σ_m 有所提高,其中 PGC-1/1 和 BGC-1/2 样品的 σ_m 分别是空白配方的 2.2 和 2.0 倍(0.48 MPa 和 0.45 MPa),且含上述扩链剂的胶片的 ε_m 在空白配方对应值的 65% ~107% 范围内波动(ε_m =63.19% ~103.42%)。因此,选择适当参数的脂肪族二元醇做扩链剂可提高粘合剂胶片的力学性能。但同时发现含 EGC、PGC、BGC 和 HGC 扩链剂的胶片均出现了增塑剂析出现象,且随其含量增加,增塑剂析出愈加严重,若应用于全配方推进剂中,硝酸酯增塑剂可能会向推进剂表面和界面迁移[7],引起装药界面脱粘,表面析油,推进剂感度提高等系列严重问题,因此在配方研究中应考虑其影响。

3.2 聚醚二元醇扩链剂对粘合剂胶片高温力学性能的影响

按照配方设计参数及实验方法制备含聚醚二元醇扩链剂的粘合剂胶片,并对其高温(+50 ℃)力学性能进行对比,试验及测试结果见表 4。

表 4 聚醚二元醇扩链剂对粘合剂胶片高温(+50 ℃)力学性能的影响

Table 4 Effects of the polyether diols on the mechanical characteristics of the binder film at 50 ℃

sample	the state and appearance of the cured films	σ_m/MPa	ε_m/%
blank	viscoelastic film with dry surface	0.22	96.81
PEG100-1/4	viscoelastic film with dry surface	0.33	94.94
PEG100-1/2		0.47	122.75
PEG100-1/1		0.39	75.07
PEG150-1/4	viscoelastic film with dry surface	0.38	89.40
PEG150-1/2		0.29	99.29
PEG150-1/1		0.25	66.88
PEG200-1/2	viscoelastic film with dry surface	0.26	111.71
PEG200-1/1		0.39	102.17
PEG400-1/2	viscoelastic film with dry surface	0.26	88.81
PEG400-1/1		0.35	67.88
PEG1000-1/2	viscoelastic film with dry surface	0.26	68.88
PEG1000-1/1		0.35	78.81

由表 4 可知,不同分子量的聚醚二元醇加入配方对粘合剂胶片的高温力学性能有明显影响,含聚醚扩链剂的配方的 σ_m 均大于空白配方的值,其中 PEG100 的 σ_m 是空白配方对应值的 2.1 倍(0.47 MPa),而 ε_m 亦随聚醚二元醇的种类、含量不同,呈现不同的变化趋势,其 ε_m 在空白配方对应值的 70% ~123% 范围内波动(ε_m =67.88% ~122.75%)。此外,胶片固化正常,表面干洁,未出现增塑剂析出等情况。

3.3 三元醇交联剂对粘合剂胶片高温力学性能的影响

按照配方设计参数及实验方法制备含三元醇交联

剂的粘合剂胶片，并对其高温（+50 ℃）力学性能进行对比，试验及测试结果见表 5。

表 5　三元醇交联剂对粘合剂胶片高温（+50 ℃）力学性能的影响

Table 5　Effects of three types of triols on the mechanical characteristics of the binder film at 50 ℃

sample	the state and appearance of the cured films	σ_m/MPa	ε_m/%
blank	viscoelastic film with dry surface	0.22	96.81
GCR-3/7	viscoelastic film with dry surface	0.23	50.56
GCR-1/1	viscoelastic film with dry surface	0.26	50.27
BTR-3/7	viscoelastic film with dry surface	0.28	70.32
BTR-1/1	viscoelastic film with dry surface	0.27	58.93
TMP-3/7	viscoelastic film with dry surface	0.29	66.99
TMP-1/1	viscoelastic film with dry surface	0.32	73.23

由表 5 可知，GCR、BTR 和 TMP 交联剂对粘合剂胶片的力学性能亦有影响，含交联剂的胶片 σ_m 比空白配方的值略有提高（0.23～0.32 MPa），且它们的 ε_m 均低于空白配方的值（50.27%～73.23%）。此外，含三种交联剂的胶片固化正常，未见增塑剂析出等情况。

3.4　含扩链和交联剂的粘合剂胶片的凝胶分析

进一步分析扩链和交联剂对粘合剂胶片高温力学性能的影响机理，分别对 BGC-1/2、PEG100-1/2 和 TMP-1/1 样品进行凝胶分析，结果见表 6。

表 6　含扩链和交联剂的粘合剂胶片的凝胶分析

Table 6　Gel fraction of the binder film with chain extender and cross linker

sample	blank	BGC-1/2	PEG100-1/2	TMP-1/1
gel fraction/%	95.2	96.4	96.7	97.3

由表 6 可知，加入扩链和交联剂的粘合剂胶片的凝胶分数均大于空白配方的值，凝胶分数的测试结果与 σ_m 的变化规律一致，即随粘合剂胶片的凝胶分数增大（交联密度增大），其拉伸强度相应提高；伸长率 ε_m 的变化规律则有不同，其中含扩链剂 BGC 和 PEG100 的胶片的 ε_m 均高于空白配方的值，而含交联剂 TMP 的胶片的 ε_m 则相应低于空白配方的值。上述不同主要由扩链剂与交联剂在调节粘合剂网络结构方面的作用机理不同引起，扩链剂在粘合剂网络中的作用与高分子粘合剂网络双模或多模非均匀形变理论[6,8]一致，即在交联网络中引入短链，形成具有适当长、短链比例的双模交联网，能有效提高体系的断裂强度和断裂伸长率；交联剂引入粘合剂网络体系能与固化剂反应提高体系交联密度和微相分离程度[9]，使 σ_m 提高 ε_m 降低，但在 NEPE 推进剂中由于大增塑比的作用使微相分离作用变弱[4,5]，因此，粘合剂胶片的 σ_m 略有增加，而 ε_m 相应降低。

4　结　论

（1）脂肪族二元醇扩链剂使 NEPE 推进剂粘合剂胶片的力学性能有所提高，但会引起硝酸酯增塑剂析出。

（2）选择适当种类、含量的聚醚类二元醇可显著提高粘合剂胶片的高温力学性能。

（3）三元醇交联剂能使粘合剂胶片的 σ_m 有所提高，ε_m 降低。

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Fracture Behavior of HTPB Composite Propellant in Ⅰ-Ⅱ Mixed Mode Crack

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Abstract: HTPB composite solid propellant containing slant internal cracks under uniaxial tensile load were measured by using of material testing device WDN-10KN, with the tensile rate of 2 mm · min^{-1}. The whole progress of Crack propagation was recorded by camera. Curves of the Loading-Displacement, crack initiation angle and fracture loading were obtained. By comparison with series fracture criteria including T-Criterion, S-Criterion, σ_θ-Criterion, the crack initiation angle of solid propellant obtained is in approximately agreement to that from T-Criterion, showing that the T-Criterion can be used as a theory prediction to the crack initiation angle of the composite solid propellant.

Key words: solid mechanics; HTPB composite propellant; Ⅰ-Ⅱ mixed mode crack; crack initiation angle

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Effects of Chain Extenders and Cross Linkers on Mechanical Characteristics of Binder Film of NEPE Propellant at High Temperature

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Abstract: The effects of chain extenders and cross linkers on the mechanical characteristics of the binder film of the NEPE propellant at 50 ℃ were experimentally studied. The results indicate that the aliphatic and low molecular polyether diols (chain extenders) improves the mechanical characteristics of the binder films at high temperature, and the three types of triols (cross linkers) increases the maximum stress of the binder film and decreases the maximum elongation of the bind film. It is found that the aliphatic diols might cause the exudation of nitrate esters from the binder film during the curing process.

Key words: solid mechanics; chain extender; cross linker; NEPE propellant; binder system; mechanical characteristic