

橡胶表面碳基薄膜耐磨改性研究进展^{*}

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摘要: 橡胶具有良好的压缩性和回弹性及良好的气密性、耐溶剂性等性能,是航空航天、石油化工、汽车工业等领域必不可少的密封材料。然而,实际服役中其因摩擦因数极高(≥ 1)而易磨损失效,进而引发密封介质泄漏,严重影响设备安全性及服役寿命。类金刚石碳基薄膜由于其高硬度、化学惰性、低摩擦磨损特性等被认为是最有前景的橡胶表面耐磨改性涂层。一方面,通过调整薄膜沉积参数可以控制薄膜灵活度和沉积温度,足够的灵活度要求薄膜能够适应橡胶软基底形变而不会发生崩落,而低的沉积温度可以避免降解或破坏橡胶基底;另一方面,碳基薄膜的化学成分(主要包括碳和氢)与橡胶展现出极好的相容性,可以确保其良好的结合强度。综述了近 20 年来橡胶表面碳基薄膜耐磨改性研究的重要结果和最新进展,总结了目前研究中尚未解决的问题及未来的研究方向。

关键词: 碳基固体润滑薄膜; 橡胶材料; 摩擦学性能; 研究进展; 发展趋势

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Research Progress on Wear Resistance Modification of Carbon-based Film on Rubber

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Abstract: Rubber is widely used as an essential sealing material in aerospace, petrochemical industry, automotive industry and other fields due to its good compressibility and resilience, airtightness, solvent resistance and so on. However, it is easy to wear out due to its high friction coefficient (≥ 1) in actual service, which leads to leakage of sealing medium, and seriously affects the safety and service life of the equipment. Diamond-like carbon (DLC) based films are considered to be the most promising wear-resistant coatings for rubber due to their high hardness, chemical inertness and low friction and wear. The flexibility and deposition temperature of DLC film can be controlled by adjusting the deposition parameters, sufficient flexibility of the film is required to adapt large deformations of rubber substrates without falling off, while the low deposition temperature can avoid degradation or damage to the rubber substrate. The chemical composition of DLC film (mainly composed by C and H) exhibits a good compatibility with rubber materials, which can ensure its good adhesion. The important results and the latest research progress on the wear resistance of carbon-based film on rubber in the past two decades were summarized, and the unsolved problems in the current research and the future research trends were pointed out.

Keywords: carbon-based film; rubber; tribological performance; research progress; development tendency

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0 前言

现代工业设备中存在大量的密封装置^[1-2],用以防止工作介质泄漏及外界灰尘和异物侵入。密封介质一旦泄漏,轻则造成物料流失、设备损坏,重则可能引发火灾、爆炸。大多数动密封泄漏事故均与密封件的密封失效有关^[3-5]。橡胶具有良好的压缩性和回弹性、气密性等优异性能,是最常用的密封材料。橡胶动密封件装入密封槽后受到高压介质挤压变形,与钢质槽壁和密封杆对磨的摩擦因数极高($\mu \geq 1$),高摩擦产生的摩擦热极易导致橡胶密封件软化而快速磨损失效^[6-8],使得高压密封介质从受损部位渗漏,影响设备的安全可靠服役。因此,改善橡胶密封件的抗磨损性能具有重大的工程意义。

目前,橡胶耐磨改性的方法主要包括:整体改性和表面改性。整体改性是改变橡胶本体分子结构^[9]或添加纳米固体润滑剂^[10](如石墨^[11]、石墨烯^[12]和二硫化钼^[13]等)。整体改性对橡胶基础胶料的性能影响较大,且考虑到材料摩擦磨损主要发生在其表面或亚表面。因此,表面改性是提高橡胶耐磨损特性的理想方法之一。表面改性分为表面化学改性^[14]和表面物理改性^[15]。表面化学改性是指通过表面化学反应使材料表面化学组分、结构发生改变以减小界面黏着。化学改性方法主要包括表面卤化^[16-17]、表面磺化^[18]、表面氧化^[19]等。表面化学改性能降低橡胶表面摩擦,但化学改性层厚度较薄($0.01 \sim 10 \mu\text{m}$),摩擦耐久性差。

表面物理改性主要包括等离子处理^[20-22]和硬质薄膜^[23-25]。等离子处理主要是通过高能等离子体轰击橡胶表面,改变其表面物理和化学性质,从而改善其摩擦磨损性能。但等离子处理层同样存在厚度薄(几十纳米)和摩擦耐久性差的问题。硬质薄膜改性研究工作主要分为三类:

(1) 金属薄膜。白俄罗斯国立理工大学 TASHLYKOV 等^[23]将金属薄膜(Ti、Cr 和 Mo 等)沉积在橡胶表面,结果发现金属薄膜对消除滞后摩擦效果甚微,且其与钢对偶存在强烈的黏着,导致其摩擦因数较高。

(2) 陶瓷薄膜。英格兰谢菲尔德大学 GHASSEMIEH 等^[24]研究表明,碳化钨薄膜可有效降低滞后摩擦,但其高硬度会对钢对偶造成严重犁沟摩擦,导致摩擦因数急剧升高($0.4 \sim 0.5$)。

(3) 类金刚石碳薄膜。类金刚石碳薄膜(DLC)

具有与橡胶良好的化学相容性(两者主要成分均为碳和氢)、与钢质对偶的低黏着特性、机械硬度可控、结构多变(如多微纳结构、多元素掺杂等)、低摩擦磨损等性能^[26-27],是橡胶表面耐磨改性最理想的硬质薄膜材料。

近年来,橡胶表面碳基薄膜耐磨改性的研究工作受到了学术界和工业界的广泛关注。本文将重点综述近 20 年来橡胶软表面硬质碳薄膜耐磨改性的主要结果和最新研究进展,并指出了目前研究中仍需解决的关键问题及未来的研究趋势。

1 橡胶表面碳薄膜耐磨改性研究进展

自 1971 年 AISENBERG 等^[28]首次制备类金刚石碳薄膜以来,经过近 50 年的发展其研究形成了完整的体系。根据薄膜结构和成分差异可分为六大类^[29-30]:①无氢非晶碳基薄膜(a-C);②无氢四面体非晶碳基薄膜(ta-C);③掺杂类无氢非晶碳基薄膜(a-C:X,X 为金属或非金属元素);④含氢非晶碳基薄膜(a-C:H);⑤含氢四面体非晶碳基薄膜(ta-C:H);⑥掺杂类含氢非晶碳基薄膜(a-C:H:X,X 为金属或非金属元素)。除此之外,通过向非晶碳薄膜中引入纳米结构,可得到不同结构非晶碳基薄膜如类富勒烯碳薄膜^[31-33]、类洋葱碳薄膜^[34-35]、纳米金刚石的非晶碳基薄膜^[36-37]等。本文所涉及的 DLC 薄膜,未经特殊说明均指 a-C:H 族薄膜。

1.1 橡胶基底前处理及典型的沉积技术

1.1.1 橡胶基底前处理

橡胶表面存在大量污染物(包括油、脂及粉尘颗粒等),为避免其对薄膜结合强度的影响,有必要对橡胶基底进行清洗。清洗过程主要利用超声清洗机在蒸馏水^[38-39]、有机溶剂^[40-43]、有机溶剂+水^[44-57]或肥皂水+水^[58-62]中反复清洗,然后利用气流^[38-39]或 UV 光照^[41]干燥备用。清洗结束后,为进一步提高薄膜膜基结合强度,需要对橡胶基底进行等离子体轰击预处理,所选用的等离子体源主要包括氩气^[40,43,54,56-59,63-68]、氢气^[69]、氩气+氢气^[44-55,60]、氧气^[61-62,70]和臭氧^[41]等。

1.1.2 橡胶基底前处理

橡胶表面 DLC 薄膜沉积技术主要包括 PACVD^[40,44-48,50-51,55,71]、PECVD^[49,62-63,72-73]、P-CVD^[52-53,59-60,69]、磁控溅射^[42,58,74-75]等。除此之外,还包括一些特殊的沉积技术如飞秒脉冲激光^[76]、PBII^[41]、ETP-CVD^[54]、GLAD^[43]等。前驱气体主要包括 $\text{Ar}+\text{C}_2\text{H}_2$ 、 $\text{Ar}+\text{CH}_4$ 或 Ar 直接溅射石墨靶等。

特殊碳源的使用主要是为了获得掺杂类 DLC,如利用 $\text{Si}(\text{CH}_3)_4$ 得到 Si-DLC 薄膜^[41],利用 $\text{Si}(\text{CH}_3)_3-$

$\text{O-Si}(\text{CH}_3)_3$ 得到 $\text{SiOx-DLC}^{[71]}$ 薄膜等。表 1 给出了橡胶表面 DLC 薄膜沉积技术等相关信息。

表 1 不同弹性体基底前处理及表面 DLC 薄膜沉积技术等信息

Table 1 Pretreatment of different elastomer substrate and DLC film deposition technology

Substrate	Cleaning	Plasma pretreatment	Deposition technology	Gases and precursors	Interlayer/Films	Ref.
Q, CR, NBR	—	H_2	RF-PCVD	CH_4	DLC	[69]
Q	Distilled water	—	T-FAD	C_2H_2 , CH_4 , C_2H_2	DLC	[38-39]
Butyl rubber	Acetone	Ar	RF-PACVD	CH_4	DLC	[40]
Silicone rubber	—	—	FSPLD	Frozen $\text{C}_5\text{H}_{11}\text{OH}$	DLC	[76]
Fluoro rubber	Ethanol	Ozone	PBII	$\text{Si}(\text{CH}_3)_4$	Si-DLC	[41]
FKM, HNBR	Ethanol	—	UBRMS	$\text{Ar}+\text{C}_2\text{H}_2$	Cr/WC/W-DLC	[42]
FKM, HNBR, ACM	—	—	UBRMS	$\text{Ar}+\text{C}_2\text{H}_2$	WC/W-DLC	[74]
HNBR	—	—	UBRMS	$\text{Ar}+\text{C}_2\text{H}_2$	Ti-DLC	[75]
HNBR	Soap+demineralized water+hot water	Ar	CFUBMS	$\text{Ar}+\text{C}_2\text{H}_2$	DLC	[58]
HNBR	↑	Ar	P-CVD	$\text{Ar}+\text{C}_2\text{H}_2$	DLC	[59]
HNBR	↑	Ar/Ar+ H_2	P-CVD	$\text{Ar}+\text{C}_2\text{H}_2$	DLC	[60]
ACM	Detergent+boiling water	Ar→Ar+ H_2	PACVD	$\text{Ar}+\text{C}_2\text{H}_2$	DLC	[44-49]
HNBR	↑	Ar/Ar+ H_2	PACVD	$\text{Ar}+\text{C}_2\text{H}_2$	DLC	[50-51]
HNBR	↑	Ar→Ar+ H_2	P-CVD	$\text{Ar}+\text{C}_2\text{H}_2$	DLC	[52]
HNBR	↑	Ar/Ar+ H_2	P-CVD	$\text{Ar}+\text{C}_2\text{H}_2$	DLC	[53]
NBR	↑	Ar	ETP-CVD	$\text{Ar}+\text{C}_2\text{H}_2$	DLC	[54]
ACM	↑	Ar→Ar+ H_2	PACVD	$\text{Ar}+\text{C}_2\text{H}_2$	DLC	[55]
NBR	—	Ar	CFUBMSIP	$\text{Ar}+\text{C}_4\text{H}_{10}$	SiC/DLC, Si-DLC	[64-67]
TPU	Ethanol	—	RF-MS	Ar, C_4H_{10} , C_2H_2	DLC	[77]
NBR, FKM, TPU	Soap+hot water	O_2	P-DC MS+PACVD	$\text{Ar}+\text{C}_2\text{H}_2$	DLC	[61]
NBR	Soap+hot water	O_2	MS+PECVD	$\text{Ar}+\text{C}_2\text{H}_2$	DLC	[62]
NBR	Detergent+boiling water	Ar	DC-MS	Ar (Graphite)	DLC	[56]
↑	↑	↑	MS	↑	DLC	[57]
↑	Soap+ethanol+hot water	↑	RF-MS	↑	Ti-C/DLC	[68]

(1) Q(硅橡胶), CR(氯丁橡胶), NBR(丁腈橡胶), HNBR(氢化丁腈橡胶), EPDM(三元乙丙橡胶), ACM(丙烯酸酯橡胶), FKM(氟橡胶), TPU(热塑性聚氨酯弹性体橡胶)。

(2) RF(射频), DC(直流), P-DC(脉冲直流), T-FAD(T形滤波电弧沉积), FSPLD(飞秒脉冲激光沉积), PACVD(等离子体辅助化学气相沉积), PECVD(等离子增强化学气相沉积), GLAD(掠角沉积), ETP(扩展热等离子体沉积技术), CFUBMSIP(闭合场非平衡磁控溅射离子注入), UBRMS(非平衡反应磁控溅射)。

1.2 表面形貌及特征

2004年, NAKAHIGASHI等^[69]制备出一种灵活性极高的 DLC 薄膜(F-DLCTM),并将其成功应用于相机伸缩镜头处 O 形密封圈。此后,日本学者普遍认为橡胶表面 DLC 薄膜表面裂纹的存在是其具有灵活性的主要原因^[38-40, 76, 72],并尝试利用模板法人制造裂纹^[40],但对裂纹的形成机理并不清楚。

直到 2008 年, BUI 等^[58, 75]研究不同等离子预处理偏压和薄膜沉积偏压对橡胶表面 DLC 薄膜结合力的影响时发现,不同等离子预处理偏压和薄膜沉积偏压会导致薄膜沉积前后的温度差异,从而影响薄膜裂纹密度。此后, PEI^[60]和 MATINEZ-MATINEZ^[44-45]等采用不同预处理偏压和薄膜沉积偏压来控制薄膜沉积时的温差,制备出了表面结构完全不同的薄膜。此外,薄膜沉积温差存在正温差、

零温差和负温差。温差($|\Delta T|$)越大,薄膜裂纹密度越高,且负温差时薄膜裂纹密度相对正温差时更高。

2010 年, MATINEZ-MATINEZ^[44]等对裂纹的形成机理进行了详细探讨。正温差时($T_{\text{end}} > T_{\text{start}}$),橡胶基底在整个沉积过程中处于不断膨胀状态,沉积初期薄膜呈柱状生长且相互分离。然而,随着温度逐渐达到平衡,橡胶基底的膨胀速率减慢,而薄膜的生长速率恒定。因此,从某一时刻开始薄膜逐渐呈连续生长。随着温度进一步增加,橡胶基底持续膨胀,导致薄膜受拉应力作用而碎裂(即裂纹产生)。待沉积结束后,由于橡胶基底从沉积结束时的高温逐渐降至室温的过程中会发生收缩,导致薄膜板块相互挤压而向内弯曲;负温差时($T_{\text{end}} < T_{\text{start}}$),随沉积温度逐渐降低,橡胶基底不断收缩,薄膜为应对压应力作用而形成褶皱状形貌;当温差为 0 时($T_{\text{end}} =$

T_{start}), 由于薄膜沉积中温度没有变化, 即橡胶基底无膨胀和收缩, 因而薄膜为连续薄膜无裂纹产生。

2012 年, PEI 等^[50] 进一步指出, 正温差时薄膜较平整, 裂纹向内弯曲。负温差时薄膜板块向上隆起呈拱形, 裂纹向内弯曲。即橡胶表面 DLC 薄膜的裂纹均向内弯曲, 这种向内弯曲且闭合的裂纹一方面可以防止裂纹尖锐边缘与摩擦对偶的剧烈碰撞, 有效避免犁沟摩擦和磨粒磨损; 另一方面, 裂纹的存在还可以作为微存储器储存润滑剂和磨屑。此外, 薄膜沉积前后的温差 ($|\Delta T|$) 越大, 薄膜板块尺寸越小。

尽管裂纹的存在对薄膜结合强度(缓解应力)和灵活性(应对形变)至关重要, 但也能在一定程度上降低薄膜机械强度^[63]。因此, 部分学者提倡在橡胶表面发展褶皱状连续薄膜。这种结构能够改变薄膜光学带隙, 在制备光学器件方面存在潜在的应用价值^[43]; 能够影响表面疏水性^[71]、哺乳动物细胞功能^[63]等, 在生物医药领域具有潜在的应用价值; 能够降低摩擦实际接触面积, 从而显著降低摩擦和磨损^[61]。

1.3 橡胶/薄膜灵活性和结合强度

橡胶表面 DLC 薄膜灵活性及结合强度是决定薄膜润滑功能的两个极其重要的参数。灵活性用以应对橡胶基底受外力变形而造成的薄膜崩落, 其主要采用反复弯曲法定性判定, 即对橡胶/DLC 薄膜样品向外或向内反复多次弯折^[67], 然后在光学显微镜或电子显微镜下观察其脱落情况。DLC 薄膜表面裂纹的存在是决定其灵活性的关键, 因为当样品发生变形时, 侧向裂缝会释放应力而不会分层, 导致 DLC 薄膜可随橡胶变形而不会发生脱落。

高的结合强度可确保薄膜能够牢固黏附在橡胶表面起到润滑作用。由于橡胶基体的黏弹性特性, 常规的测量方法如划痕法受到限制。目前, 主要采用两种定性方法测试橡胶表面 DLC 薄膜结合强度, 即 X 切割法和拉伸法。X 切割法是利用刀片在样品表面切出 X 形切痕, 然后利用特定的胶带黏接并撕拉切痕, 最后通过显微镜观察切痕处薄膜的脱落情况^[65, 78]。拉伸法则是对样品进行一定程度的拉伸, 并考察拉伸前后薄膜板块尺寸的变化。如果橡胶基底与 DLC 薄膜结合强度足够高, 拉伸结束后可在薄膜表面观察到更多的裂纹; 如果结合强度较差, 除了产生新裂纹外, 在裂纹边缘薄膜会剥落以释放应力^[59]。SCHENKEL 等^[46] 曾提出了定量计算橡胶表面 DLC 薄膜结合强度的方法, 即薄膜结合力 $\tau =$

$4t\sigma/I_d$, 而 $I_d \approx 3/4 L$, 其中 t 和 σ 分别为薄膜厚度和抗拉强度(一般为 720 MPa), L 为最大拉力作用下薄膜板块尺寸的平均值。尽管该方法可用来定量估算橡胶表面 DLC 薄膜结合力, 但利用最大拉力下最大板块对角线的平均长度来计算板块尺寸从统计学上讲并不准确^[79]。

橡胶与 DLC 薄膜结合强度受众多因素影响, 如基底洁净程度及薄膜应力强弱等。对橡胶基底进行清洗以除去其表面污染物(如油脂、蜡及粉尘颗粒等)可有效改善薄膜结合强度^[44, 46, 50, 52]。

清洗结束后, 对橡胶表面进行等离子预处理可增强薄膜结合强度, 但等离子体种类存在差异。NAKAHIGASHI 等^[69] 采用氢等离子体预处理, MASAMI 等^[41] 采用臭氧作为等离子体源, KIM 等^[70] 和 STHIRUMALAI 等^[61-62] 采用 O_2 作为等离子体源, 而 LUBWAMA 等^[64-67] 和 WEN 等^[56-57, 68] 和 DE HOSSON 等^[44-53, 55, 60] 则分别采用 Ar 和 $Ar+H_2$ 作为等离子预处理气体。而 ZHANG 等^[73, 80] 研究发现惰性氩等离子体预处理能明显改善薄膜结合强度, 这归因于氩等离子体能够打断丁腈橡胶表面 C-H 键形成大量悬键, 这些悬键能够与碳薄膜沉积时的碳原子键合形成化学键而提高薄膜结合强度。

此外, 设计过渡层也可提高薄膜膜基结合强度。2008 年, PEI 等^[42] 尝试采用 Cr 做中间层, 结果发现 Cr 中间层的存在不利于薄膜膜基结合强度。2009 年, LACKNER 等^[77] 则提倡发展质软且高弹的类聚合物碳薄膜作为中间层。通过有限元分析发现, 这种中间层不仅具有高承载能力, 而且具有与软基底较高的结合强度。2012 年, LUBWAMA 等^[64] 引入了 Si-C 层作为中间层, 并发现 Si-C 中间层的存在会增加上层薄膜中 sp^2 含量, 有利于缓解薄膜内应力, 从而提高膜基结合强度^[65]。但遗憾的是, Si-C 中间层的引入不利于提高薄膜摩擦磨损性能。2019 年, WU 等^[68] 引入了 Ti 掺杂碳薄膜作为中间层, 结果表明适当偏压沉积的中间层能够有效增强薄膜结合强度。同年, QIANG 等^[81] 引入了 Si 层作为中间层, 研究了 Si 中间层厚度对丁腈橡胶表面 Si-DLC 薄膜结合强度的影响。结果表明, Si 中间层厚度存在最优值($\sim 1.04 \mu m$), 过薄或过厚均不利于薄膜结合强度。Si 中间层厚度影响薄膜内应力(sp^2 含量), 进而影响薄膜结合强度。

另外, 使用闭合场非平衡磁控溅射技术也能提高薄膜结合强度^[64-67], 因为该技术能够致使薄膜沉积时高能粒子轰击橡胶基体使其表面致密化并减少

薄膜残余应力^[66-67]。

1.4 橡胶表面碳薄膜摩擦学性能

表 2 总结了不同橡胶基底表面不同薄膜摩擦参数、摩擦因数等信息。总体而言,沉积 DLC 薄膜

后其摩擦因数比原始橡胶摩擦因数要低,这主要归因于 DLC 薄膜的化学惰性,其有效阻止了钢对偶与橡胶基底的直接接触,从而避免了严重的黏着摩擦。

表 2 不同橡胶基底表面不同薄膜摩擦参数、摩擦因数等

Table 2 Friction conditions and friction coefficients, etc of different film on different rubbers

Samples		Tribological properties					Ref.
Substrate	Films	Counterpart	Load/N	Speed/(cm/s)	Lubr.	COFs	
Q, CR, NBR, EPT	DLC	Al	0.1	1	Dry	0.7~1.3	[69]
Butyl rubber	DLC	Steel	0.5~5	10	Dry	0.15~0.25	[40]
Fluoro rubber	Si-DLC	Steel(SUJ)	0.49	1	Dry	0.2~0.25	[41]
FKM, HNBR	Cr/WC/W-DLC	Steel(100Cr6)	1	10	Dry	0.2~0.6	[42]
FKM, HNBR, ACM	WC/W-DLC	↑	1~5	↑	↑	0.2~0.6	[74]
HNBR	Ti-DLC	↑	1,3	↑	↑	0.17~0.25	[75]
HNBR	DLC	↑	1,3	↑	↑	0.16~0.22	[58]
HNBR	DLC	↑	1,3	↑	↑	0.16~0.22	[59]
HNBR	DLC	↑	1	↑	↑	0.11~0.18	[60]
ACM	DLC	↑	1~5	↑	↑	0.07~0.3	[44]
ACM	DLC	↑	1,3	5~40	↑	0.16~0.30	[46]
ACM	DLC	↑	1~5	10	Dry, oil	0.07~0.3	[49]
HNBR	DLC	↑	1~5	10	Dry	0.1~0.22	[51]
HNBR	DLC	↑	1	10~30	↑	0.11~0.18	[52]
HNBR	DLC	↑	1,3	10~50	↑	0.11~0.23	[53]
NBR	DLC	↑	1~3	10	↑	0.2~0.3	[54]
ACM	DLC	Steel(100Cr6)	0.001~1	5	↑	0.05~0.4	[55]
NBR	SiC(optional)/DLC or Si-DLC	WC-Co	1, 5	10	Dry or water	0.18~0.6	[64~67]
NBR, FKM, TPU	DLC	Steel(100Cr6)	1	10	Dry	0.3~0.65	[61]
NBR	DLC	Steel(100Cr6)	1	10	Dry	0.2~0.3	[62]
NBR	DLC	WC	0.3	~4.7	Dry	0.22~0.37	[56]
↑	DLC	WC	0.3	~4.7	Dry	0.05~0.30	[57]
↑	Ti-C/DLC	ZrO	0.3	~3.1	Dry	0.15~1.00	[68]

1.4.1 橡胶表面碳薄膜的摩擦

2010 年, PEI 等^[59-60]发现薄膜板块尺寸越小(裂纹密度越高),摩擦因数越小,达到稳定摩擦状态所需的时间越短。此外,作者否定了掺杂类 DLC 薄膜在橡胶表面的应用,因为掺杂的纳米颗粒与碳原子形成的硬质陶瓷纳米相可能会对对偶材料造成犁沟摩擦而导致高磨损。同年, MATINEZ-MATINEZ 等^[44]发现所有薄膜摩擦因数随摩擦距离增加而逐渐增加,这可能与橡胶基底的黏弹性有关,导致了对偶与薄膜间摩擦接触面积和形状的差异。

2011 年, SCHENKEL 等^[46]研究了薄膜不同时间间隔的摩擦行为。经较短时间间隔(24 h)摩擦时薄膜起始摩擦因数逐渐增加,而经 144 h 间隔后继续摩擦时薄膜起始摩擦因数则完全相同,这可能是由于经 144 h 间隔后橡胶又恢复到了原始状态。这些结果间接地证实了薄膜摩擦因数随摩擦距离增加而逐渐增加可能与摩擦对偶压入样品深度有关。而且,摩擦因数随着摩擦载荷和速度增加而增加,更高

速度下摩擦因数增加越快,因为橡胶基底可能没有足够的时间恢复到前一状态。这些行为均表明橡胶表面 DLC 的摩擦行为可能与橡胶基底的黏弹性密切相关。同年, MATINEZ-MATINEZ 等^[47]发现,薄膜摩擦因数曲线与对偶压入样品的深度曲线同步。基于此,作者基于 Maxwell 模型和 Voigt 模型引入了标准线性模型(SLS 模型),模拟计算了刚性圆球对橡胶基压入深度的变化情况。结果显示,刚性圆球对橡胶基底的压入深度变化值随压入次数的增加逐渐减小并趋于稳定。而在模拟实际摩擦过程中对偶压入深度时,作者对上述模型进行了修正(双 Voigt 模型)。研究表明,随摩擦的进行,对偶压入深度逐渐增加并趋于稳定。然而,随着研究的逐步深入^[48],作者通过模拟计算和试验观察到了摩擦对偶接触形状的不对称性(即球斑呈椭圆形),这是因为摩擦前次形变未恢复,使得其形变面积超出了橡胶与对偶的实际接触面积(不完全接触)。这种情况严重地削弱了橡胶黏弹性对薄膜摩擦因数的作用

(滞后摩擦),这意味着试验所观察到的摩擦因数随摩擦距离增加而逐渐增加的原因,不仅与橡胶的黏弹性有关,而且还与摩擦界面的黏着摩擦有关。

2012 年, MATINEZ-MATINEZ 等^[49]通过设计不同的摩擦试验,即在对偶表面沉积 DLC 薄膜和油环境下摩擦试验发现在上述两种情况同时存在时薄膜的摩擦因数最低,并且所有薄膜在油润滑条件下的摩擦因数最终随着摩擦距离的增加而逐渐降低,这进一步证实了黏着效应是薄膜摩擦因数总体增加的主要原因。

同年, PEI 等^[51]还对黏着摩擦和滞后摩擦对薄膜总体摩擦的贡献大小进行了详细分析。黏着摩擦主要依赖于摩擦接触面积,而滞后摩擦则依赖于接触面力的大小(或扭矩大小)。此外,研究还发现,摩擦过程中薄膜受法向摩擦应力作用会发生二次脆断,这对工程应用极为不利,会造成新产生锋利边缘与摩擦对偶的强烈碰撞,造成犁沟摩擦和磨粒磨损。此外,增加摩擦界面剪切力,滞后摩擦和接触面积不变,黏着作用增加,总体摩擦因数增加;增加载荷,黏着摩擦降低,滞后摩擦和接触面积增加,总体摩擦因数增加。这意味着两种不同的薄膜沉积在同一橡胶表面,相同摩擦条件下的摩擦因数差异主要取决于摩擦界面剪切作用的强弱。

同年, LUBWAMA 等^[64]引入了 Si-C 层作为中间层,但用摩擦因数曲线斜率来判断薄膜失效速率时,发现其失效速率从大到小依次为 Si-C/Si-DLC>Si-C/DLC>Si-DLC>DLC^[65],即 Si-C 中间层的引入不利于提高薄膜摩擦磨损性能,这主要归因于 Si-C 中间层的存在降低了薄膜的显微硬度。

2014 年, LUBWAMA 等^[67]详细研究了上述薄膜的灵活性和水环境下的摩擦学行为。低载下对偶材料硬度影响薄膜的摩擦行为,且无论干摩擦还是水环境薄膜磨损并无差异;高载下对偶材料硬度并不影响其摩擦行为,但不同环境下其摩擦行为存在差异性。干摩擦时,只有 Si-C/Si-DLC 薄膜具有优异的抗磨损特性。水环境下,所有薄膜均具有优异的抗磨性。摩擦热计算结果表明,摩擦表面结构转变主要是形成致密的磨屑层而不是摩擦热导致的石墨化现象。

2016 年, THIRUMALAI 等^[61]将 DLC 薄膜沉积在三种不同的聚合物(丁腈橡胶、氟橡胶和热塑性聚氨酯)表面,研究发现高表面能有利于摩擦转移膜的形成,从而显著降低摩擦学性能。

2018 年, THIRUMALAI 等^[62]将 DLC 薄膜沉积在 NBR 表面,并研究了氧等离子预处理和两种不同

的沉积方法(类物理气相沉积和类化学气相沉积)对薄膜摩擦学性能的影响。结果显示,氧等离子预处理橡胶表面能有效降低薄膜摩擦因数,而类物理气相沉积技术制备的薄膜具有更加优异的摩擦学性能。

同年, LIU 等^[56]研究了氩气气压对 NBR 表面 DLC 薄膜摩擦学性能的影响。结果表明,氩气气压存在最优值(1.4 Pa),此时薄膜具有最优的摩擦学性能,这主要归因于薄膜中高的 sp^3 含量及其表面能。同年, LIU 等^[57]还研究了沉积偏压对 NBR 表面 DLC 薄膜摩擦学性能和密封性的影响。研究显示,当薄膜沉积偏压为-200 V 时,具有最优的摩擦学性能,这主要是由于薄膜相对高的机械硬度。而理论计算与试验结果表明,薄膜优异的密封性则主要是由其杨氏模量和粗糙度协同作用的结果。

2019 年, WU 等^[68]引入了 Ti 掺杂碳薄膜作为中间层,并研究了中间层沉积偏压对薄膜摩擦学性能的影响。研究结果表明,合适偏压沉积的中间层能够有效增强薄膜摩擦学性能。

2020 年, QIANG 等^[82]研究了基底偏压对丁腈橡胶表面有无 Si 中间层的 Si-DLC 薄膜的摩擦学性能影响。当偏压较低时(≤ 500 V),有无 Si 中间层对薄膜摩擦性能影响不大,但磨损机理完全不同。当偏压较高时(> 500 V),有 Si 中间层的薄膜具有更低的摩擦因数和磨损率,因为上层薄膜的力学性能改善,且 Si 中间层作为承载层降低了薄膜脆断的风险。

1.4.2 橡胶表面碳薄膜的磨损

尽管有学者尝试采用三维轮廓仪定量测定薄膜磨损率^[64-65,68],但由于橡胶本体所具有的黏弹性特征,其表面 DLC 的磨损率无法准确定量,而是采用典型的定性方法,即通过光学显微镜或扫描电子显微镜观察薄膜摩擦后的磨痕形貌^[75](被严重磨平还是局部抛光)。采用定性法评价薄膜磨损存在明显的局限性,因为当薄膜抗磨损性差别不大时无法准确比较其强弱,相关讨论存在争议。

2 结论与展望

橡胶表面 DLC 基薄膜表面存在大量裂纹,这主要与薄膜沉积前后的温差有关。裂纹的存在一方面可以提高薄膜灵活度以应对橡胶基底弹性形变而不会发生脱落,另一方面可以释放薄膜应力以提高其结合强度。薄膜结合强度可以通过橡胶基底前处理(清洗和等离子轰击预处理)及引入中间层得到有效改善。橡胶表面 DLC 薄膜摩擦性能由黏着摩擦

和滞后摩擦共同决定。

目前,相关研究领域仍然存在亟待解决的关键问题:

(1)定量困难。作为耐磨改性涂层,橡胶表面 DLC 薄膜的结合力和抗磨损性是决定其服役寿命的关键参数。然而,由于橡胶柔性基底自身的黏弹性形变,这两种性能目前还没有一种准确的定量评价方法。

(2)摩擦因数较高。橡胶表面 DLC 薄膜摩擦因数均大于 0.1(与载荷有关),远远高于硬质基底表面 DLC 薄膜摩擦因数($\sim 10^{-3}$ 量级)。

(3)裂纹密度与密封性关系缺乏研究。前期研究表明,薄膜裂纹密度越高其摩擦因数越低。但裂纹密度越高,薄膜机械强度损失越严重,密封介质泄漏的通道越多。

为了推动 DLC 薄膜在橡胶密封领域的广泛应用,可考虑从以下几个方面开展研究工作:① 探寻准确测定橡胶表面 DLC 薄膜结合强度和磨损量的定量方法,科学预测其耐磨寿命;② 对比研究橡胶与硬质基底表面碳薄膜摩擦磨损行为与机理的差异性,探究硬质基底表面 DLC 薄膜超低摩擦的本征结构因素及摩擦界面结构演变行为,指导构筑橡胶表面 DLC 薄膜低摩擦界面;③ 准确控制薄膜表面裂纹密度,研究不同裂纹密度对薄膜摩擦学行为和密封性的影响机制,指导裂纹密度在摩擦性能和密封性能之间的合理取舍。

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