Wear of Liquid Crystal-Additivated Polymers Against Steel

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ABSTRACT: A thermotropic liquid crystal, 4,4'-dibutylazobenzene, added in a 1% weight proportion to thermoplastic materials, polystyrene (PS) and styrene acrylonitrile (SAN), gives, after molding the mixture at 150°C and 22 MPa, a new family of polymers with an improved resistance to sliding dry wear against steel as tested in a pin-on-disc tribometer. Variable load, sliding speed, and distance tests were performed to establish the range of conditions under which the wear-resistance improvement is maximum. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 831–837, 1999

Key words: sliding wear; polymer–steel contact; liquid crystal–polymer blends; antiwear additives; pin-on-disc

INTRODUCTION

Since the early 1950s, synthetic materials have been increasingly replacing ferrous and nonferrous alloys as machine elements.¹ Polymers and polymer composites are now being used as engineering materials for applications where tribological properties are important.² Thus, the use of polymers and polymeric composites in seals and bearings as well as in power transmission systems is rapidly increasing.³ Recently, a new class of self-reinforcing polymeric materials based on blends of isotropic thermoplastics and thermotropic liquid crystal polymers has been developed.⁴

Dispersions of low molecular weight liquid crystals and polymers are also known,⁵ especially those where the concentration of polymer is near 50% and

the liquid crystal is separated out in the form of randomly distributed droplets. These materials are called polymer-dispersed liquid crystals (PDLCs) and are currently under development for several electrooptical applications such as switchable windows, high-definition projection systems, large flatpanel displays, and light shutters for optical signal processing. The attempts to use liquid crystals as reinforcing agents have only shown moderate effects upon mechanical properties such as elasticity modulus or tensile strength.⁶

We have recently described the preparation⁷ and use⁸ of azo and cyanoaryl thermotropic liquid crystals as additives to lubricants to reduce the friction and wear of steel-steel and steel-aluminum pairs. As some of these liquid crystals are to some extent miscible with thermoplastic polymers, an extension of the utility of these additives could be to improve the wear resistance of the polymers when sliding against steel. As far as we are aware, this is the first time classic (nonpolymeric) liquid crystals have been added to polymers in order to act as antiwear additives.

In the work reported here, two base polymers [polystyrene (PS) and styrene acrylonitrile (SAN)] were used with the same additive, 4,4'-dibutylazo-

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	TT 1	Roughness (µm)		
Material	(Shore D)	R_t	R_a	
100% PS	78	1.9 - 2.9	0.1 - 0.4	
100% SAN	84	1.8 - 5.2	0.3 - 0.75	
99% PS + 1% LC1	83.9	1 - 3.4	0.2 - 0.4	
99% SAN +1% LC1	85	1 - 5.4	0.15-0.55	

Table IHardness and Roughness of Pure andAdditivated Polymers

 $R_{t}, {\rm maximum}$ peak-to-valley roughness; $R_{a}, {\rm arithmetic}$ average roughness.

benzene, in a 1% weight ratio, and tribological experiments were carried out in a pin-on-disc machine with a steel pin sliding against a polymer counterface. 4,4'-Dibutylazobenzene was chosen due to its ease of preparation and purification,⁷ relatively low cost, and good performance as an antifriction and antiwear lubricating oil additive.⁸

EXPERIMENTAL

Materials

The hardness and roughness of starting and additivated polymers are shown on Table I. Glass transition temperatures for the pure polymers and blends were determined by differential scanning calorimetry in a Perkin–Elmer DSC-6. Addition of 1% 4,4'-dibutylazobenzene to PS and SAN does not significantly change the hardness and surface roughness of the polymers (see Table I). Also, no changes in the thermal behavior of the polymers were detected by differential scanning calorimetry. Glass transition temperatures, T_g (°C): 112 (PS); 72 (SAN), are in agreement with the literature values.⁹

4,4'-dibutylazobenzene was prepared as described.⁷ Polymer discs were obtained by pressing the powders at 22 MPa while heating them at 150°C in a Buehler metallographic press. Pins were made of AISI 52100 steel as previously described.⁸

Tribological Experiments

An Implant Science ISC-200PC pin-on-disc tribometer was used, with the following fixed experimental parameters: temperature: $23 \pm 1^{\circ}$ C; wear track radius (*R*): 11.0–11.7 mm; and pin end

spherical radius (r): 0.8 mm. The influence of normal load, linear speed, and distance on the friction behavior and wear loss was studied by fixing two of these three variables and changing the third. For each polymer disc, three tests were carried out under each set of parameters, and medium values of volume loss were taken. The friction coefficients were continually recorded as a function of time.

A JEOL 6100 SEM microscope was used and the material for examination was prepared with the aid of a Bio-Rad Polaron Division sputter coater evaporation unit. The thickness of the deposited gold film was approximately 600 Å.

Wear tracks were measured by image analysis with an Olympus BH metallographic microscope connected to an Optimas image analyzer. Volume loss (Figs. 1–6) is the result of measuring the wear track width and applying eq. (1) as described in ASTM G99 standard¹⁰:

$$V = 2\pi R \left(r^2 \sin^{-1} \frac{d}{2r} - \left(\frac{d}{4} \right) (4r^2 - d^2)^{1/2} \right) \quad (1)$$

where R is the wear track radius; d, the wear track width; and r, the pin-end radius. The values of the wear track width used are the mean values of 30 measures.



Figure 1 Wear data for PS and PSLC under variable load.



Figure 2 Wear data for PS and PSLC under variable speed.

RESULTS AND DISCUSSION

A preliminary test¹¹ carried out with the following set of parameters: load: 0.49 N; sliding speed: 0.1 m/s; and distance: 1000 m, showed a decrease



Figure 4 Wear data for SAN and SANLC under variable load.

in volume loss for the additivated polymers, although a slight increase in friction coefficients was observed for the liquid crystal-polymer blends. These results moved us to carry out variable conditions tests in order to determine the



Figure 3 Wear data for PS and PSLC under variable sliding distance.



Figure 5 Wear data for SAN and SANLC under variable speed.



Figure 6 Wear data for SAN and SANLC under variable sliding distance.

conditions under which minimum wear and/or friction is obtained for the blends when compared with the unadditivated polymers, thus establishing the real usefulness of the additive.

The friction coefficients (see Tables II and III) and volume losses (Figs. 1-6) show analogous behavior for pure as for additivated polymers. Both friction and wear (with some exception in the case of the copolymer SAN) increase with increasing loads.

Increasing loading leads to greater penetrations of the metal asperities into the polymer matrix and to increase in the adhesive junction size, which leads to larger volumes of material wear debris.¹² Under a high load condition, the extruding effect of the hard counterpart to the softer polymer should also be considered.

Wear variations with increasing sliding speed are more complex: While PS and PS liquid crystal (PSLC) show a general trend of increasing wear with speed, SAN and SAN liquid crystal (SANLC) show an initial increase in volume loss to reach a maximum at 0.10 ms⁻¹ and a further decrease from 0.10 to 0.20 ms⁻¹. It is important to notice that variable speed tests were carried out under different normal loads for each polymer (0.25 N for PS and PSLC, and 0.49 N for SAN and SANLC).

The effect of the sliding velocity is particularly important because of the viscoelastic response of

the different thermoplastics to changes in the strain rate together with the effect of any temperature changes at the sliding interface. The initial rise in the wear rate has been attributed to an increasingly brittle response of the polymer which is unable to plastically deform. Further increments in sliding velocity lead to an increase of the temperature at the interface and an increased plasticity. Eventually, the thermal effects become dominant and wear rates fall.¹² Under the experimental conditions studied here, this effect is only observed for SAN and SANLC but not for PS or PSLC, thus suggesting that, in these latter cases, the point where thermal effects are predominant has not been reached. Volume loss clearly increases with growing sliding distance, although

Table IIFriction Coefficients for PS and PSLCUnder Variable Conditions

Load = 0.25 N; Distance = 1000 m				
	Friction	Coefficient		
(ms ⁻¹)	PS	PSLC		
0.025	0.64	0.60		
0.05	0.70	0.70		
0.10	0.55	0.65		
0.15	0.60	0.61		
0.20	0.69	0.68		

Sliding Speed = 0.15 ms^{-1} ; Distance = 1000 m

	Friction	Coefficient
Load (N)	PS	PSLC
0.01	0.32	0.28
0.25	0.60	0.61
0.34	0.69	0.72
0.49	0.78	0.67
0.73	0.96	0.87

Load = 0.25 N; Sliding Speed = 0.15 ms^{-1}

	Friction	Coefficient
Distance (m)	PS	PSLC
1000	0.60	0.61
2000	0.60	0.58
3000	0.62	0.57
4000	0.64	0.57
5000	0.65	0.58

Sliding Speed	Friction	Coefficient		
(ms ⁻¹)	SAN	SANLC		
0.025	0.93	0.66		
0.05	0.82	0.79		
0.10	0.78	0.82		
0.15	0.76	0.75		
0.20	0.78	0.77		

Table III	Friction	Coefficients	for	SAN	and
SANLC UI	ıder Varia	able Conditi	ons		

 $I_{\text{odd}} = 0.40 \text{ N}$

Sliding Speed = 0.15 ms	⁻¹ ; Distance = 1000 m
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Load (N)	Friction Coefficient		
	SAN	SANLC	
0.25	0.35	0.37	
0.49	0.76	0.75	
0.98	0.83	0.78	
1.96	0.82	0.82	
3.43	0.90	0.83	

Load =	0.49	N;	Sliding	Speed	=	0.15	ms^{-1}	1
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	Friction Coefficient		
Distance (m)	SAN	SANLC	
1000	0.76	0.75	
2000	0.81	0.79	
3000	0.86	0.84	
4000	0.85	0.87	
5000	0.89	0.87	

friction coefficients remain practically unchanged.

Maximum wear reductions are reached in the case of PS for $v = 0.15 \text{ ms}^{-1}$, L = 0.49 N, and d = 1000 m, under which PSLC gives a volume loss more than 60% lower than that of the unadditivated polymer. Similar reductions are observed for SANLC with respect to SAN under the same set of variables, although, in this case, wear reductions higher than 60% are also observed for $v = 0.15 \text{ ms}^{-1}$, L = 0.49 N, and d = 2000 m and for $v = 0.15 \text{ ms}^{-1}$, L = 0.25 N, and d = 1000 m.

From the experiments carried out, it can be concluded that the liquid crystal additive could not be called an internal lubricant in the sense that it is not able to significantly lower friction coefficients in the range of conditions studied here. However, this liquid crystal clearly acts as an antiwear additive, with improvements in wear resistance for SAN, with $v = 0.15 \text{ ms}^{-1}$ and L = 0.49 N, between 38 and 63% in the whole range of sliding distances.

Practical utilization of polymers in machine sliding components and other tribology-related applications depends, to a considerable extent, on the understanding of the ways in which their wear behavior is influenced by the imposed operating conditions. The wear process involves a number of complex interactions, but it can be considered to be caused by the energy created by the frictional work and released during sliding within the contact zone.¹³ In the case studied here, the contact configuration is formed by a rigid asperity traversing a deformable polymer substrate.

A major factor in the good wear performance of many plastics is the formation of beneficial tribofilms¹⁴ (i.e., transfer and third-body films). This is often the case when the counterface is either a ceramic or a metal. Consequently, additional lubrication is generally not needed or desirable in these cases. To enhance this self-lubricating behavior, additives such as PTFE, graphite, or MoS₂ are often added to a base polymer to provide an antiwear or bearing grade.

The base polymers used in this work have low self-lubricating properties and poor wear resistance. The presence of the liquid crystal additive can reduce wear but does not improve their selflubricating characteristics as no significant reduction was observed in the friction coefficients.

The nature of the transfer film has a profound influence on tribological behavior. If a permanent transfer film is formed, further volume loss of the material will be limited, since no further bulk material will be needed to replenish the film. If the transfer film formed is poor and continuously sloughs off, more and more bulk material will be used, resulting in a high wear rate.²

As can be seen by the series of micrographs (Figs. 7 and 8), the wear process of the polymer disc appears after repeated sliding on the wear track until the generation of fragments of wear debris (Fig. 9). The main wear mechanisms could be assumed to be a combination of adhesive and abrasive wear, although from the observation of worn surfaces and wear debris, softening and extruding wear processes appear also involved. As a significant fraction of wear debris remains trapped in the wear track, this leads to the for-



Figure 7 SEM micrograph of SAN/LC blend wear track.

mation of a layer of highly deformed material covering extensive portions of the wear track, thus protecting subsequent layers of material from being torn off.

CONCLUSIONS

This is the first time a classical (nonpolymeric) liquid crystal has been shown to improve the tribological properties of polymers. 4,4'-Dibutylazobenzene, in a 1% proportion, forms homogeneous mixtures with PS and SAN. This low concentration was selected in order to establish the viability of this new antiwear additive; however, as the additive concentration in the blend is an important factor, we are currently studying the behav-



Figure 8 SEM micrograph of SAN/LC blend wear track showing generation of wear debris fragments.



Figure 9 Wear debris from SAN/LC blend wear track.

ior of blends with a variable concentration of liquid crystal added.

Variable experimental conditions and tribological tests were carried out to asses the limits of the new additive. While friction coefficients remain virtually unchanged with the presence of the additive, wear resistance measured as volume loss can be more than 60% lower than that of the pure polymers.

Variable speed tests showed different behaviors for PS and SAN, both pure and additivated. These differences are attributed to the different thermal properties of the two polymers. Further work is necessary in order to establish the influence of these additives on the mechanical properties of the polymers and thus the range of applications.

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