Using Silicone Masterbatch for Controlling the Friction Coefficient of Polyacetal gears

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Abstract: As the automotive technologies continue to progress, more and more electronic components are being used in car modules to assist the car driver in many aspects of safety. Once installed, these electronic modules need to function correctly during the life cycle of the car, thus they must be well protected against harsh environment, moisture and outgassing contaminants.

For that reason, there is an increasing concern about using plastic materials as they can potentially leach out volatile species that can condense over electronic components of the car. One typical example is the use of plastic gears as the alternative to metallic gears. Plastic gears can be smaller, lighter and have higher accuracy than metal gears. Their manufacturing processes are much simpler and of lower cost than the analogous metallic gears. As any gear, plastic gears need lubricants for noise and vibration damping when they are in motion.

Dow Corning developed a series of silicone based masterbatches that show very good lubrication properties when added in small amounts to the plastic resin, such as polyacetal, during compounding and injection molding. Silicone masterbatches lower the friction coefficient and enable the use of the plastics in the most demanding applications, such as office appliances, gears, conveyor belts, bearings or medical tubing connectors.

In this paper, we discuss the effect of free silicone species on electronic and electrical contacts in cars. We show also that silicone masterbatches contain a very low level of volatile species, far below the threshold level for getting any adverse effect on electronic or electric components in the car. Finally, we discuss the correlation found between the complex viscosity of these masterbatches with the friction coefficients of their POM compounds.

Keywords: Silicone, Masterbatch, Friction Coefficient, HMB-1103, BY 27-219, MB50-002, MHE/GC/FID, Car electronics, Polyacetal, POM

1 Introduction

Polyoxymethylene (POM), also known as Polyacetal, is a thermoplastic resin that features low friction coefficient, low wear properties, good fatigue and creep resistance and exceptional dimensional stability. It can be used in a number of applications in high-tech domains that require precision and durability. Because of its intrinsic low friction coefficient it is widely recommended in areas where self-lubricating is required, such as bearings[1], medical device connectors, electronic appliances, conveyor belts[2] and small gears[3]. Pure POM compounds are generally used in applications of low sliding speeds, low loads or short time exposure to friction[4]. For high speeds, high loads or for application with a long term exposure to friction and wear, additional lubricants are necessary. In this case, the lubricant can be spread over the surface of the part to mitigate the sliding[5]; it can also be pre-blended with the plastic resin before making the part to become an internal lubricant[6]. Silicone based additives are used in these situations, and when they are used, species with high vapor pressure can potentially offgas from their matrix and deposit everywhere in the surrounding environments[7]. This is a big issue for electronic contact components in cars[8] or for car body painting[9]. Thus, it is important to control the level of low molecular weight silicone species to limit this

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adverse effect. However, there are a limited number of public studies that discuss the levels that can lead to failure. In a recent paper[10], the minimum content level that leads to adhesion failure was determined by ATR FTIR spectroscopy for Dow Corning 200 silicone Fluid spread over gold or aluminum plates. The authors observe that the failure occurs when the silicone level is as low as 0.5–64 μg/cm^2. The determination of the contamination threshold for the electronic parts failure is more complex but has also been discussed[11]. In this study, the effect of silicone is said to depend on several factors including the silicone structure, its molecular weight and vapor pressures. These factors are said to define the silicone transfer mechanisms. In this study, the authors calculated the silicone contamination level in a confined space at given pressure conditions. We think that this calculation is probably realistic for liquid silicone (conformal coatings) but not for silicone masterbatches which are solid pellets[12]. For fast cure conformal coatings, the threshold level for electrical motors, potentiometers and relay failures is reported to be around 10 ppm in the air [11], but for silicone masterbatches, the data are not available, at least not in public literature. This explains why we decided to run this study. We hypothesized that volatile species can be transferred to electronic components through the air, which leads to silicone contamination. In this case, the partial pressure of each volatile species present in the masterbatch should be taken into account when determining the threshold level.

In this paper, we have determined the level of major volatile components in a typical masterbatch (MB40-006), calculated their vapor pressures at room temperature and their concentration in a confined space of one cubic meter. This is a worst case scenario since a car interior volume is not confined. Our work demonstrates that silicone masterbatches contain a very low level of silicone volatile species. Their partial pressure is so low that their concentration is far below the threshold level for getting any adverse effect on electronic or electric components present in the car interior. The paper discusses also the performances of some commercial silicone masterbatches such as HMB-1103, BY 27-219, MB50-002, MB40-006 as additives for low friction coefficient of POM compounds.

2 Experimental

2.1 Raw Materials

MB40-006 is a Dow Corning silicone masterbatch containing ultra high molecular silicone gum diluted into polyacetal matrix.

HMB-1103 is a Dow Corning silicone masterbatch obtained by reactively extruding silicone gum with polyetheylene methacrylate copolymer.

BY 27-219 is a Dow Corning silicone masterbatch also obtained by partially reacting silicone gum with polyetheylene methacrylate copolymer as HMB-1103 but has lower complex viscosity than the latter.

MB50-002 is a Dow Corning silicone masterbatch obtained by extrusion blending of silicone gum with polyethylene.

All silicone masterbatches were used as obtained from Dow Corning laboratories.

2.2 Experimental procedure

2.2.1 MHE/GC/FID

Multiple Headspace Extraction GC with Flam Ionization detector is used for the analysis of volatile organics in solid, liquid and gas samples[13]. The popularity of this technique has grown over recent years and has now gained worldwide acceptance for analyses of volatile species in plastics[14]. In this case, a sample of 0.2 g is placed into a vial and heated at 220 °C. Volatile species are then extracted and sent into a GC column, followed with a FID detector.

2.2.2 Preparation of polyacetal compounds

To measure the flexural modulus and friction coefficient, the silicone masterbatch and POM pellets are directly pre-blended at the desired concentration and injection molded using the molding conditions described in Dupont Delrin grades molding guide[15].

2.2.3 Measurement of Friction Coefficient (CoF)

The CoF was measured using a tribometer equipped with dry ball/plan set up at room temperature. We used a POM ball of 12.37 mm in diameter. The plan was prepared with the POM containing various masterbatch samples at a given concentration (length: 125 mm, width: 13 mm, thickness: 1.6 mm). All experiments were done with a normal load of 12.5 N, corresponding to a contact pressure of 70 MPa. Translation speed: 8 mm/s, over a distance of 14 mm, total cycles: 700. Every sample was run twice and the data in Figure 2 represent the average.

Table 1. *MHE/GC/FID Analysis of 6 samples of MB40-006*

Reference	% D4	% D5	% D6	Total %
MB40-006 (1)	0.264	0.417	0.352	1.033
MB40-006 (2)	0.118	0.279	0.289	0.687
MB40-006 (3)	0.141	0.323	0.31	0.774
MB40-006 (4)	0.097	0.25	0.244	0.591
MB40-006 (5)	0.149	0.367	0.346	0.862
MB40-006 (6)	0.126	0.327	0.324	0.777
Average (%)	**0.13**	**0.31**	**0.3**	**0.74**

Table 2. *Level of cyclic siloxane in a confined space of 1^3 containing 100 g of the POM compound loaded with 3 % of MB40-006.*

Average (%)	**0.13**	**0.31**	**0.30**	**0.74**
Cyclics content in the compound at 3% loading	0.004	0.009	0.009	0.022
Boiling Point (°C)	176	210	245	
Molecular weight (gr/mole)	296	370	444	
Molar fraction at 3% loading (%) (Row 9/Row11)	1.279E-05	2.507E-05	2.045E-05	
Vapor Pressure at 25°C (mmHg) for a pur material, calculated from its Bp and Bp calculator	2	0.99	0.48	
Vapor Pressure at 25°C (mmHg) for the compound	2.55811E-07	2.48196E-07	9.81405E-08	
Partial Pressure at 25°C (atm) for the compound (use Row 12)	3.36593E-10	3.26573E-10	1.29132E-10	
Volume (M^3)	1	1	1	
Temperature (K)	298	298	298	
Moles per M^3 (PV=nRT)	1.35856E-13	1.31812E-13	5.21205E-14	3.19788E-13

3 Results and Discussion

3.1 Level of cyclic siloxane in MB40-006

Table 1 shows the level of cyclic siloxane determined by the MHE/GC/FID analysis of 6 samples of MB40-006. The data show an average of 0.74 % of 2,2,4,4,6,6,8,8-Octamethylcyclotetrasiloxane(**D_4**), 2,2,4,4,6,6,8,8,10,10-decamethycyclopentasiloxane(**D5**), 2,2,4,4,6,6,8,8,10,10,12,12-dodecamethycyclohexacyclosiloxane(**D6**) that can potentially offgas the matrix.

In general, this masterbatch is recommended for use at 3 % maximum in a polyacetal compound. Thus, one can calculate the level that is expected to be in the POM compound after dilution.

As can be seen from *Table 2*, the level of cyclic species present in a confined space of one cubic meter at room temperature and normal pressure can be determined as follows:

From the level of cyclic species in a POM compound loaded with 3 % of MB40-006 and the molecular weight of each cyclic species, we can calculate the molar fraction (n) of each cyclic siloxane in the compound. The vapor pressure of pure cyclic siloxane is determined using the partial pressure calculator *http://www.trimen.pl/witek/calculators/wrzenie.html*. Using the ideal gas law (P V= n R T), the partial pressure of each cyclic species can be determined. The data obtained are used to determine the level of free volatile species that can potentially be present at room temperature and normal pressure in a confined space of one cubic meter. This is a working hypothesis, since the volume of a car interior is not confined and is not one cubic meter. From this calculation, we found 4.02 10-5 ppm of D_4 cyclics, 4.88 10^{-5} ppm of D_5 cyclics and 2.31 10^{-5} ppm of D_6 cyclics which is less than 10^{-4} ppm of total cyclic siloxanes. This is too far below the threshold value (10 ppm) to be worried about electric or electronic contact failure. *Figure 1* shows the graph of a relay contact failure as a function of cyclic content. Here, 10 g of cured silicone was put in a closed environment in the proximity of relays

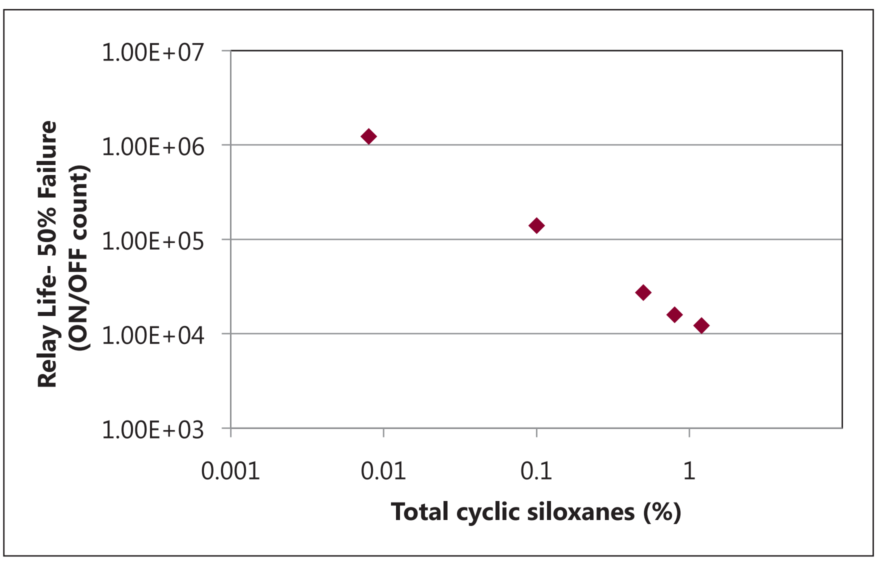

Figure 1. *Graph of relay contact failure as a function of cyclic siloxane content.*

Table 3. *MHE/GC/FID Analysis of 6 samples of POM compounds containing less than 5 % of MB40-006.*

Samples	% D_4	% D_5	% D_6	Total %
MB40-006 Compound 1	0.003	0.004	0.003	0.009
MB40-006 Compound 2	0.0025	0.004	0.002	0.0085
MB40-006 Compound 3	0.003	0.004	0.003	0.010
MB40-006 Compound 4	0.003	0.003	0.003	0.009
MB40-006 Compound 5	0.003	0.004	0.004	0.011
MB40-006 Compound 6	0.003	0.002	0.003	0.008

operated at 24 V/24 mA at 5 Hz on/off cycles. The points on the graphs represent the number of cycles to observe 50 % of failure with 8 relays. Although they are not generated in the same conditions, these data illustrate the effect of silicone on relay contact failure and are used as our reference.

In order to validate this calculation based on cyclic siloxanes present in a confined space of one cubic meter, a series of POM compounds containing less than 5 % of MB40-006 silicone masterbatch was prepared and analyzed by MHE/GC/FID to quantify the cyclic silicone level after compounding. Results are shown in *Table 3*.

The data obtained here show that siloxane volatiles generated from a POM compound containing less than 5 % of MB40-006 are in the same range as what has been calculated using the vapor pressure of the D_4, D5 D6 cyclic siloxane components. All are around 0.003 %, thus near the detection limit of the MHE/GC/FID technique (0.001 %). Although we have used MB40-006 for this study, further work, not detailed in this paper, confirmed that other masterbatches such MB50-002, HMB-1103 or BY27-219 also have a volatiles level as low as MB40-006. We concluded that any of these masterbatches can be added to POM compounds and used to make electronic parts without being worried about electric or electronic contact failures.

3.2 Effect of Silicone masterbatches on Friction Coefficients of POM compounds.

In a POM compound containing silicone masterbatches, the siloxane component is reported to migrate and phase segregate on the surface of the plastic[16]. This leads to the creation of a surface with a lower friction coefficient without compromising the bulk properties of the resin. In this study, we compared the friction coefficient and the flexural modulus of POM compounds containing MB40-006, MB50-002, BY 27-219 and HMB-1103 at the same level of the silicone fraction. As can be observed from Table 3, these silicone masterbatches substantially reduce the friction coefficient compared to the reference. Unmodified POM exhibits a CoF of 0.4515 at the steady state after 100 cycles in our testing conditions, which shows good agreement with the values available in literature[17]. For all masterbatches in the table, the CoF varies from 0.046 to 0.029 at the steady state, which is much lower than that of the unmodified POM. The flexural modulus decreases by 13 % in the worse case scenario (example 3: POM+MB50-002 in Table 4).

Figure 2 shows that the CoF decreases as a function of complex viscosity G* of the material. This is very typical of reactive masterbatches. In a separate study, we showed that the complex viscosity of these masterbatches is proportional to the level grafting reaction between silicone polymer and the polyolefin[18]. In this series, we found out that the higher the grafting ratio, the higher is the complex viscosity and the lower is the friction coefficient of the resulting POM compound, but the system reaches

Table 4. *Comparison of Mechanical Properties (Flexural modulus in Mpa) and Friction coefficient of POM compounds containing silicone masterbatches*

				Friction Coefficient per number of cycles				
Reference	**Base**	**Silicone Content %**	**Flexural Modulus**	**50**	**100**	**200**	**400**	**700**
POM Derlin Pur		0	3100	0.3005	0.4515	0.4665	0.4695	0.46475
POM + MB40-006	POM	2	2895	0.00405	0.04	0.039	0.0435	0.04063
POM+ MB50-002	PE	2	2712	0.04	0.0435	0.041	0.0395	0.041
POM+BY 27-219	EMMA	2	2768	0.038	0.0385	0.0415	0.0485	0.044
POM+HMB-1103 (1)	EMMA	2	2764	0.031	0.0295	0.029	0.0295	0.02925
POM+HMB-1103 (2)	EMMA	2	2740	0.031	0.031	0.0305	0.033	0.03163
POM+HMB-1103 (3)	EMMA	2	2740	0.0345	0.034	0.035	0.0445	0.0385
POM+HMB-1103 (4)	EMMA	2	2740	0.033	0.0315	0.0305	0.0375	0.03313

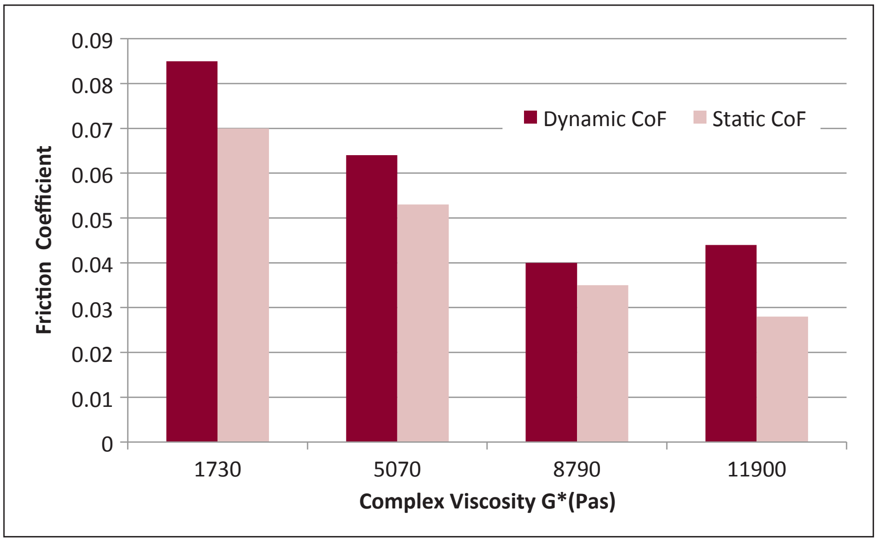

Figure 2. *Variation of Friction Coefficient as a function of complex viscosity (G*) for HMB-1103*

a lower friction coefficient plateau around 0.03.

4 Conclusions

Silicone masterbatches are widely used to reduce the friction coefficient of POM based parts, such as office appliance gears, conveyor belts, bearings or medical tubing connectors. There has been some concern that these materials can outgas volatile species that can be an issue for electronic and electrical relays.

This work shows that silicone masterbatches contain a very low level of volatile silicones that can outgas from the compound and contaminate electronic or electric components. Adding silicone masterbatches in a POM compound slightly lowers the flexural modulus of the material, but the effect is within the levels that make the material still usable (1–5 % of silicone fraction). For HMB-1103, the friction coefficient (CoF) is correlated with the rheology (complex viscosity) of the material: the higher the complex viscosity the lower the friction coefficient. Dow Corning has a wide offer of silicone containing masterbatches for POM modification but HMB-1103 represents the best compromise between performance and processability to allow the use in various applications.

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Uporaba silicijevih matičnih zmesi z namenom kontrole koeficienta trenja polioksimetilnih (POM) zobnikov

Razširjeni povzetek

Z razvojem avtomobilske tehnologije se v različnih avtomobilskih modulih uporablja vse več elektronskih komponent, ki voznikom omogočajo boljšo varnost in udobje. Vgrajene elektronske komponente morajo zagotavljati pravilno delovanje v celotnem življenjskem ciklu avtomobila, kar pomeni, da morajo biti dobro zaščitene pred grobimi vplivi okolja, vlago in onesnaženostjo zaradi izpušnih plinov.

Zaradi omenjenih razlogov je vedno večje povpraševanje po materialih iz plastike, ki so sposobni odstraniti hlapljive delce, ki se lahko kondenzirajo po površinah elektronskih komponent avtomobila. Plastika se vse pogosteje pojavlja v različnih oblikah, v različnih aplikacijah, eden takih primerov je uporaba plastičnih zobnikov kot alternativa kovinskim. Plastični zobniki so lahko manjši, izdelani so lahko z večjo natančnostjo kot kovinski, proizvodnja pa je enostavnejša in cenejša. Kot vsi tudi plastični zobniki potrebujejo mazanje za zmanjševanje šuma, blaženje tresljajev, zmanjšanje izgub itd.

Eden od vse bolj uporabljanih polimernih materialov je polioksimetilen (POM), poznan tudi kot poliacetal, ki je termoplastična smola z dobrimi tribološkimi lastnostmi, kot so nizko trenje, nizka obraba, velika togost, obstojnost in odlična dimenzionalna stabilnost. Zaradi nizkega trenja je zaželen na področjih, kjer je potrebno samomazanje, npr. pri ležajih, elektronskih napravah, tekočih trakovih, majhnih zobnikih, medicinskih konektorskih ceveh itd. Do sedaj je bil čisti POM uporabljen v aplikacijah, ki delujejo pri nizki hitrosti in nizki obremenitvi. Za uporabo POM-a v aplikacijah, ki so izpostavljene daljšim obremenitvam, obrabi, trenju, je potrebno material izboljšati. Lastnosti materiala lahko izboljšamo z dodajanjem različnih elementov v plastične smole v samem procesu mešanja/sestavljanja, brizganja in vlivanja.

Dow Corning je razvil serijo matičnih zmesi, ki temeljijo na siliciju. Z dodajanjem majhnih količin teh zmesi plastičnim masam, kot je poliacetal, te dobijo zelo dobre mazalne lastnosti. Problem se pojavi, ker lahko pride pri materialih z vsebnostjo silicija do izparevanja delcev z visokim izparilnim tlakom iz matrike in nalaganja teh delcev na elektronske komponente. Dosedanje raziskave so pokazale, da pride do okvar na komponentah, ko je nivo kontaminiranega silicija v mejah od 0,5 do 64 $\mu g/cm^2$. V tej raziskavi smo pokazali, da uporabljene silicijeve matične zmesi vsebujejo zelo nizek nivo silicijevih izparilnih delcev, veliko pod nivojem, ki naj bi povzročal škodo na elektronskih in električnih komponentah v avtomobilu. Poleg nivoja najbolj hlapljivih komponent smo v raziskavi računali izparilni tlak pri sobni temperaturi in koncentracijo teh delcev v končnem prostoru. Rezultati so pokazali, da z dodajanjem matičnih zmesi Dowa Corninga v POM vplivamo tudi na znižanje koeficientov trenja. Kar pomeni, da silicijeva matična zmes znižuje koeficient trenja in omogoča uporabo plastike v najzahtevnejših aplikacijah.

Ključne besede: silicij, POM, matične zmesi, kontaminacija, koeficient trenja, avtomobilska elektronika