

The Effect of Glass Fiber and Coupling Agents in the Blends of Silicone Rubber and Liquid Crystalline Polymers

T. Das*, A. K. Banthia, and B. Adhikari

Materials Science Centre, Indian Institute of Technology, Kharagpur-721302, India

Hyewon Jeong and Chang-Sik Ha

Department of Polymer Science and Engineering, Pusan National University, Busan 609-735, Korea

S. Alam

Defence Materials and Stores Research and Development Establishment, Kanpur-208013, India

Received August 18, 2005; Revised March 20, 2006

Abstract: Blends of silicone rubber (VMQ) and liquid crystalline polymer (LCP) were prepared using a melt blending technique in the presence and absence of glass fiber and coupling agents. The effect of glass fiber and coupling agents on the thermal, dynamic mechanical, morphological properties and cure characteristics of VMQ/LCP blends were studied. The vinyl silane coupling agent showed a significant effect on the above mentioned properties of VMQ/LCP blends by reacting at the interface between VMQ and LCP. The viscosity of the VMQ/LCP blends decreased with the addition of a coupling agent. A substantial improvement in storage modulus of VMQ/LCP blends was observed in the presence of glass fiber and coupling agents. However, as a coupling agent vinyl silane proved to be better than amine for the VMQ/LCP-glass-containing blends. The thermal stability of the pure silicone rubber was higher than those of the blends. This high thermal stability of silicone rubber was attributed to the Si-O-Si bonds. However, the thermal stability of the blends decreased further in the presence of a coupling agent, possibly due to a decrease in blend crystallinity.

Keywords: liquid crystalline polymer, silicone rubber, coupling agent, crystallinity, blend.

Introduction

Silicone rubber is a class of polymer containing long chain polymers of methyl or methyl phenyl-polysiloxane, some times vinyl groups are also included to make it easy vulcanization. The most important and outstanding property of silicone rubber is the exceptional thermal stability and electrical properties between -80 and 250 °C. These rubbers are chemically inert, tasteless and odourless. They are not affected by light, moisture and ozone. Their electrical properties are excellent. Due to its outstanding properties silicone rubber finds applications in commercial, military fields, etc.

Silicone rubber does not have all the outstanding properties of all the rubbers and also it is costly. The tensile and tear strength of silicone rubbers are much lower than those of other rubbers. They also have low pure gum strength and adhesion to metals. The strength of the silicone rubber can be enhanced by adding fibrous fillers. However, with higher

volume content of glass fiber are generally difficult to process owing to their high melt viscosity. Other difficulties encountered in short glass fiber-reinforced polymer composites include wear of processing facility resulting from the abrasion of reinforcement and fiber breakage. In recent years thermotropic liquid crystalline polymers (LCPs) have become available and can be processed in the melt to give highly oriented structures that are largely retained on cooling and subsequent crystallization.¹⁻³ A similar improvement in the mechanical properties of the polymer can be obtained by blending it with a thermotropic liquid crystalline polymer. The rod-like molecular conformation and chain stiffness give LCPs their much vaunted self reinforcing properties that are close to those of fibre reinforced composites.⁴⁻⁹ Moreover, The LCP can function as a processing aid by reducing the viscosity of matrix polymer during compounding, thereby easing the processability.^{10,11}

The present paper reports the rheological, morphological, thermal, dynamic mechanical properties of VMQ and LCP blends in presence and absence of glass fiber and coupling

*Corresponding Author. E-mail: t_das2002@yahoo.com

agents.

Experimental

The chemical structure of the polymers used in this study is shown in Table I. Silicone rubber (VMQ) used was Silastic NPC-40 from Dow Corning (USA), thermotropic liquid crystalline polymers (TLCPs) were Vectra A 950 and Vectra A 130 (contains 30 wt.% glass fiber) obtained from Ticona (USA). The LCP has the comonomer composition of 75 mol% of hydroxybenzoic acid (HBA) and 25 mol% of hydroxynaphthoic acid (HNA). The curative used was dicumyl peroxide (Varox DCP 40C) from R.T. Vanderbilt Co. Inc. (USA). The coupling agents were vinyl triacetoxysilane (Z-6075) and *N*, β -amino-aminoethyl- γ aminopropyltrimethoxy silane (Z-6020) from Dow Corning (USA).

The mixing formulation is shown in Table II. The mixing of LCP with silicone rubber was done using a co-rotating twin-rotor high temperature internal mixer with a rotor speed of 80 rpm at 290 °C for about 5 min. Before removing the blend mixture from the mixing chamber the coupling agents were added to the VMQ/LCP blends and continued the mixing for one more minute. The blended compound was then mixed with Varox 40C at 50 °C in two roll open mixing mill and vulcanized by compression molding up to an optimum cure time at 170 °C and 20 MPa. All the technical properties were determined from the vulcanized slabs, unless otherwise stated.

Rheological parameters of the uncured blends were studied with the help of a dynamic analyzer RDA-II (Rheometrics Inc., USA) equipped parallel plate. The change in viscosity of the blends was measured by varying the amount of LCP in the blend at 300 °C and a shear rate range of 1-100 s⁻¹. The cure characteristics of the blends were studied using a Monsanto rheometer (R-100) at 170 °C. The phase morphology of the blends was studied using a scanning electron microscope (SEM) (JSM-5800 of JEOL Co.). Pellets of the blends were etched in suitable solvents for 48 hrs at high temperature, where the silicone rubber is soluble. The samples were carefully cut from test specimens and auto sputtered coated with gold within 24 hrs of testing. For studying the blend morphology elastomer phase of the blends was extracted with solvent and SEM photographs were taken.

Table I. Molecular Structures of Polymers

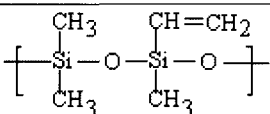
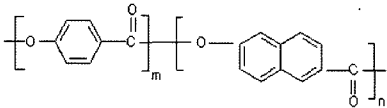
Material (Code)	Commercial Name	Molecular Structure	M_w (kg/mol)
Silicone Rubber (VMQ)	Silastic NPC40C		> 500
Liquid Crystalline Polymer (LCP)	Vectra A		> 20

Table II. Compounding Formulations

Mix. No.	A	B	C	D	E	F
VMQ	100	70	70	70	70	70
LCP (A950)	-	30	-	30	-	-
LCP (A130)	-	-	30	-	30	30
VSC (mL)	-	-	-	-	-	2
ASC (mL)	-	-	-	2	2	-
DCP (phr)	1	1	1	1	1	-

VSC-Vinyl silane coupling agent. ASC-Amine silane coupling agent.

X-ray diffraction was performed with a PW 1840 X-ray diffractometer with a copper target (Cu- K_{α}) at a scanning rate of 0.05 ° 2 θ /sec, chart speed 10 mm/2 θ , range 5,000 c/s, and a slit of 0.2 mm, applying 40 kV, 20 mA, to assess the change of crystallinity of the blends as a function of blend ratio.¹² Dynamic mechanical properties of the blends were analyzed using a TA Instrument DMA 2980 dynamic mechanical analyzer under tension clamp. The samples were subjected to a sinusoidal displacement of 15 μ m at a frequency of 1 Hz from 30 to 250 °C and a heating rate of 10 °C/min. Thermogravimetric analysis (TGA) was carried out using TGA-2100 DuPont instrument in presence of nitrogen from 100- 700 °C, with a heating rate of 10 °C/min.

Results and Discussion

Rheology. The viscosity of the VMQ/LCP blends is measured at 300 °C and the plots are shown in Figure 1. From the figure it is clear that the viscosity of the sample C is higher than that of the sample B due to the presence of glass fiber in the LCP. However, in presence of coupling agent the viscosity of these blends further decreased. This suggests that the vinyl and amine coupling agents act as lubricating agents between the VMQ and LCP phases. This reduction in viscosity is prominent when amine coupling agent is added to the blend system. With the increasing shear rate, the viscosity of the blends decreased. This is recognized to be alignment and orientation of the LCP domains themselves in the flow direction at high shear rates. This resulted in a reduction of viscosity and improved processability.¹³

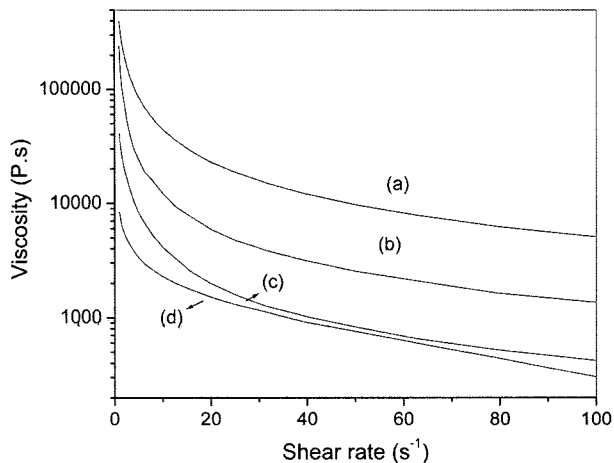


Figure 1. Viscosity as a function of shear rate for the blends: (a) C, (b) B, (c) F, and (d) E.

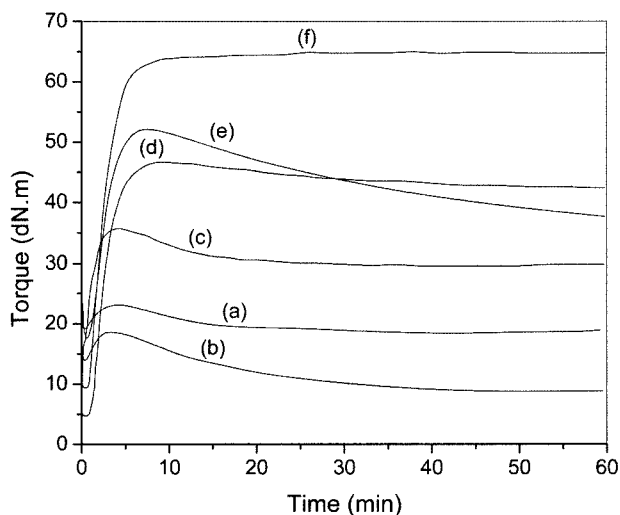


Figure 2. Rheographs of blends: (a) A, (b) B, (c) C, (d) D, (e) E, and (f) F.

Cure Characteristics. The cure characteristics of VMQ and VMQ/LCP blends are shown in Figure 2. According to the Mansanto nomenclature the minimum torque value considered as a minimum viscosity of polymer. The minimum torque, that is t_{min} , is lower in case of amine and vinyl coupling agents containing blends compare to other systems. From the figure it is clear that the samples B, D, E, and F show lower viscosity than the pure VMQ. These results are consistent with the rheological studies as aforementioned. The state of cure of the blends increased with the addition of LCP. In presence of vinyl coupling agent the VMQ/LCP (glass filled) blend show higher state of cure than all other systems. This increase is the combined effect of crosslink density and the reinforcing effect of LCP. The rate of cure in line with the state of cure suggests that the LCP accelerates

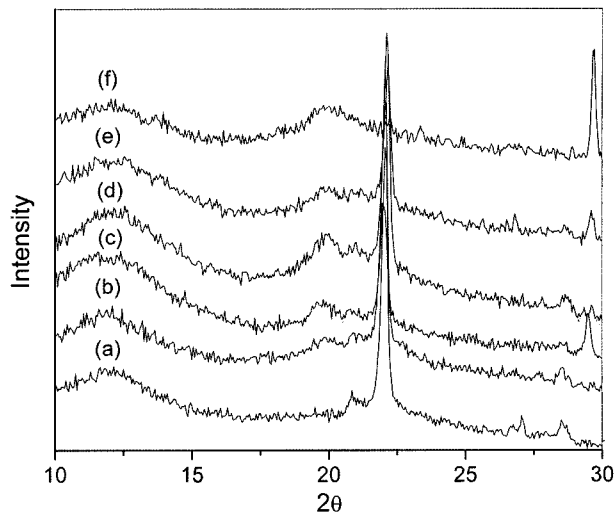


Figure 3. Wide-angle X-ray diffractograms of blends: (a) A, (b) B, (c) C, (d) D, (e) E, and (f) F.

ates the vulcanization reaction of VMQ. These results are in good agreement with the results of Shiva *et al.*¹⁴ on VMQ and LCP blends.

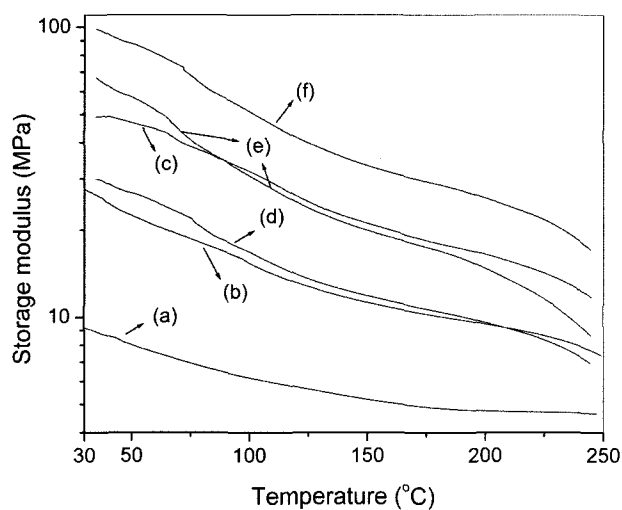
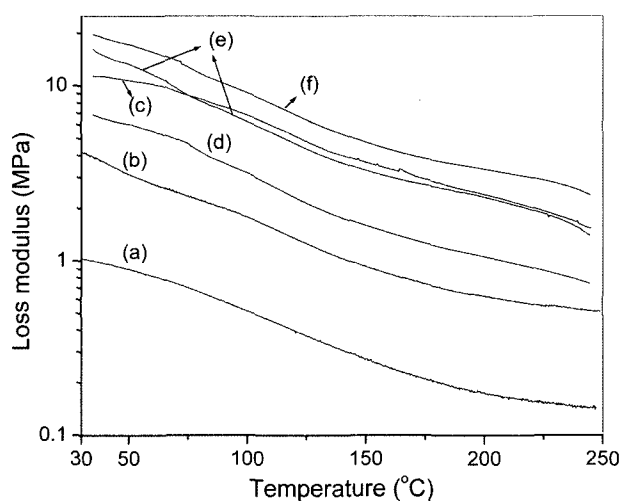
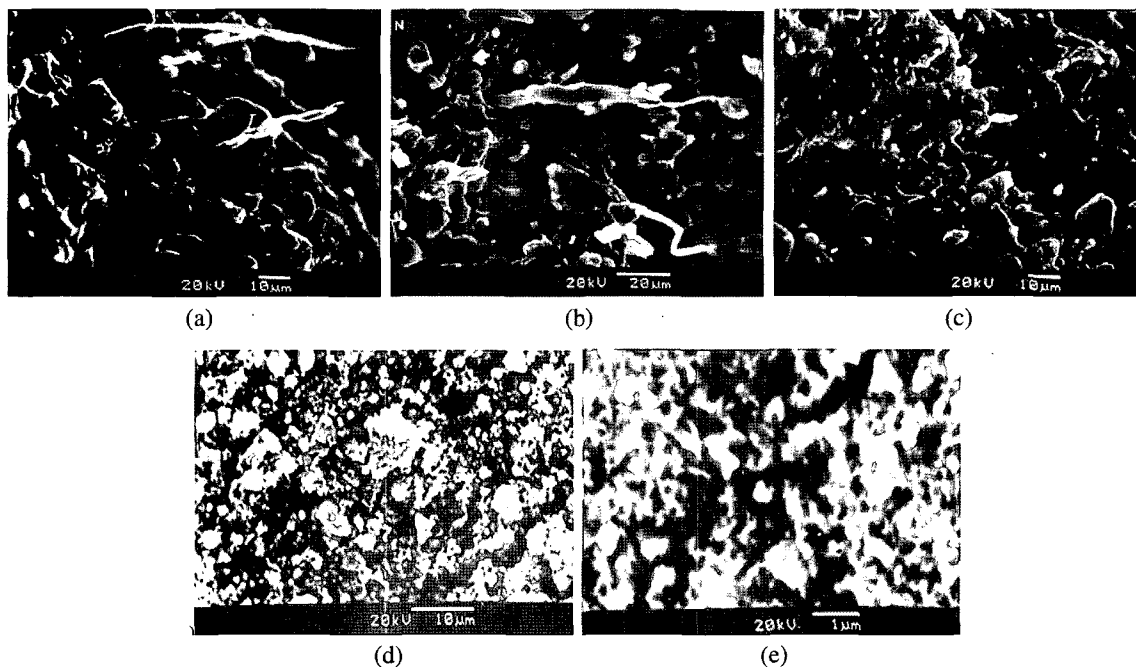
Wide-Angle X-ray Diffraction (WAXD) Measurement. The WAXD experiment was performed on uncured samples of the VMQ and VMQ/LCP blends in presence and absence of glass fiber and coupling agents and the diffractograms are shown in Figure 3. The pure silicone rubber shows a broad amorphous peak at about $2\theta = 10^\circ$ and one sharp intense peak at around $2\theta = 22^\circ$ while its blends with LCP shows another peak at about $2\theta = 20^\circ$, which is corresponding to that of the LCP phase.^{15,16} Addition of vinyl coupling agent to sample C the crystalline peak of silicone rubber at $2\theta = 22^\circ$ completely vanished and the peak corresponding to the LCP phase slightly shifted to the lower 2θ side. This indicates that the vinyl coupling agents significantly affect the ordered structure of silicone rubber by reacting at the interface between LCP and VMQ by forming graft copolymers. However the amine coupling agent shows a reduction in the intensity of the peak at about $2\theta = 20^\circ$. The percentage of crystallinity of the blends is decreased by the addition of LCP (Table III). However, this decrease is prominent in presence of coupling agents. In presence of vinyl coupling agent the VMQ/LCP (glass filled) blend shows lower crystallinity than all other systems. This suggests that the reactivity of the vinyl coupling agent towards the LCP and silicone rubber is more efficient. As it is known that the compatibilized blends crystallinity always lower than those of the un-compatibilized blends due to the random structure of the formed graft/block copolymers, which will modify the ordered structure of base polymers. Hence, the crystallinity of the blends decreases by the addition of coupling agents or compatibilizers.

Dynamic Mechanical Properties. The storage modulus

Table III. Percentage Crystallinity of the VMQ/LCP Blends

Mix. No.	Crystallinity (%)
A	28
B	22
C	11
D	16
E	11
F	7

(E') and loss modulus (E'') of the blends as a function of temperature are shown in Figures 4 and 5, respectively. The storage modulus of the silicone rubber enhanced with the addition of LCP. This improvement in E' is due to high intrinsic modulus of LCP phase, which consists of rigid rod like molecules. This enhancement is predominant in presence of coupling agents. However, the glass filled LCP shows higher storage modulus than all other system due to increase in stiffness of the polymer. From the DMA curves it is clear that the vinyl coupling agent is more effective than that of amine coupling agent for the VMQ/LCP blends. As it is observed

**Figure 4.** Storage modulus as a function of temperature for the blends: (a) A, (b) B, (c) C, (d) D, (e) E, and (f) F.**Figure 5.** Loss modulus as a function of temperature for the blends: (a) A, (b) B, (c) C, (d) D, (e) E, and (f) F.**Figure 6.** SEM photographs of blends: (a) B, (b) C, (c) F, (d) E, and (e) D.

from the Figure 6(a) that the E' value of the blends decreased with the increasing temperature. This decrease in E' is more prominent at higher level of LCP. However, the E' value of 40 wt% LCP blend nearly 2-3 times higher than the pure elastomer throughout the temperature range studied.

The loss modulus as a function of temperature is shown in Figure 5. The E'' value is higher in the case of blends when compared to pure silicone rubber. Addition of coupling agents to VMQ/LCP blends this value further increased. This increase in the loss modulus with the addition of LCP attributed to the heat buildup in the system due to friction between the VMQ and LCP fibrils under the dynamic conditions.

Phase Morphology of the Blends. The SEM micrographs of the VMQ/LCP blends are shown in Figure 6. All the micrographs show the fibrillation of the LCP domains in the matrix phase. Figure 6(a) is a micrograph of sample B shows long and very thin fibrils of LCP domains, whereas in case of sample C (Figure 6(b)) the LCP fibrillation somewhat reduced and it shows distribution of glass fibers in the matrix phase. On adding vinyl coupling agent to sample C, the phase morphology of the blend is entirely changed, which shows very short and stubby fibrils of LCP domains and these fibrils were distributed homogeneously in the matrix phase (Figure 6(c)). This change in morphology of the blend by the addition of vinyl coupling agent is attributed to the formation of graft copolymers at the interface between VMQ and LCP-glass filled. The formed graft copolymer at the interface significantly affects the morphology of the blend components. It is interesting to note that the extraction of elastomer phase is more evident in samples B and C while in presence of vinyl coupling agent the extraction of elastomer to some extent reduced. When the vinyl coupling agent is replaced with the amine coupling agent, the fibrillation of LCP is not seen, however, it shows the distribution of glass fibers (Figure 6(d)). Similar observation was also made in the case of sample D at a higher magnification. From the above results it is clear that the vinyl coupling agent is more effective than the amine coupling agent for the VMQ/LCP-glass containing blends.

Thermogravimetric Analysis. Thermogravimetry (TG) and differential thermogravimetry (DTG) curves for the blends are shown in Figures 7 and 8, respectively, and the corresponding thermal parameters are given in Table IV. From the thermograms it is clearly evident that the thermal stability of silicone rubber is higher than the LCP. This can be explained by the better thermal stability of the Si-O linkages present in the silicone rubber, compared with the ester links in the LCP. On adding LCP to VMQ, the thermal stability of silicone rubber decreased. The decrease in thermal stability of the blends is predominant in presence of glass fiber and coupling agents. This is attributed to the lower thermal stability of the amine and vinyl coupling agents. The on-set of degradations obtained from the TG curves are listed in Table IV. From the table it is clear that the pure sil-

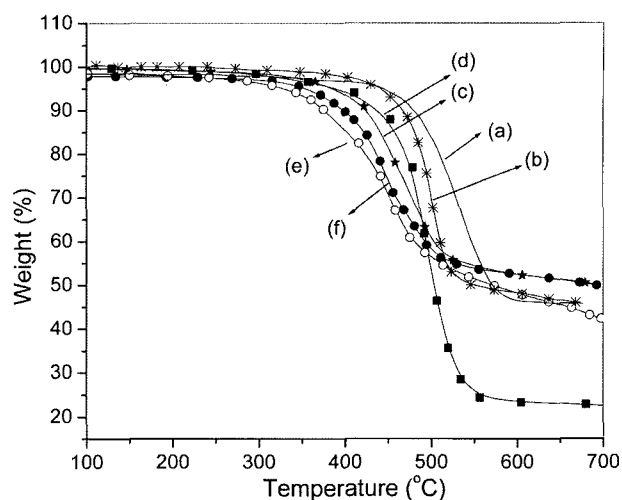


Figure 7. TG curves of blends: (a) A, (b) B, (c) C, (d) D, (e) E, and (f) F.

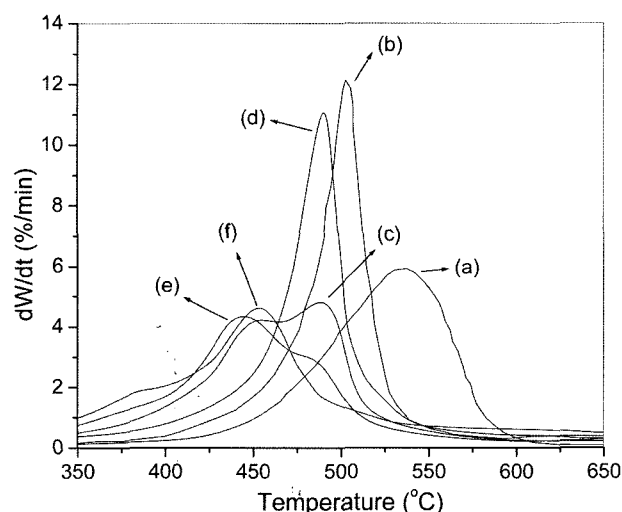


Figure 8. DTG curves for the blends: (a) A, (b) B, (c) C, (d) D, (e) E, and (f) F.

Table IV. TGA Parameters of VMQ/LCP Blends

Mix. No.	On-set Deg. Temp. (°C)	DTG Peak Temp. (°C)	dW/dt at DTG Peak Temp. (%/min)
A	445	535	5.92
B	410	502	12.14
C	369	475	4.8
D	369	490	11.06
E	339	444	4.38
F	321	454	4.65

icone rubber is thermally more stable than their blends with LCP. The on-set of degradation temperatures for the blends

with glass fiber and coupling agents are much lower than those of the VMQ/LCP blends suggesting that the glass fiber and coupling agents decreases the thermal stability of the blend. This may be due to lower thermal stability of coupling agents and decrease in crystallinity of the blends in presence of glass fiber and coupling agents. As it is known that the crystalline part of a polymer is thermally more stable than its amorphous counterpart due to high input energy required to overcome both strong intra and inter molecular interactions. Hence, the extent of decrease in thermal stability of the blends in presence of glass fiber and coupling agents is believed due to decrease in crystallinity of the blends. The DTG peak temperatures are also gives the same information. However, it is interesting to note that the rate of degradation at DTG peak temperature is high in the case of samples B and C but the samples with glass filled LCP shows lower rate of degradation. This implies that the glass fiber somewhat delays the degradation process.

Conclusions

The blends of VMQ and LCP were prepared in presence and absence of glass fiber using melt mixing procedure. The effect of glass fiber and coupling agents on thermal, dynamic mechanical, morphological properties and cure characteristics of VMQ/LCP blends were studied. The viscosity of the blends was decreased with the addition of coupling agent in presence and absence of glass fiber. This means that the coupling agents can act as lubricating agents for the VMQ/LCP blends. This is further supported by cure study. The state of cure of the blends increased in presence of glass fiber as well as coupling agents. This is attributed to be increasing crosslink density as well as reinforcing affect of glass fiber. The SEM study revealed a fine fibrillation of LCP domains in the matrix phase. However, in presence of glass fiber the characteristic fibril nature of LCP was somewhat reduced.

The coupling agents significantly affected the phase morphology of the blends due to the interaction at the interface between VMQ and LCP. The thermal stability of the silicone rubber decreased with the addition of LCP, which is further decreased in presence of glass fiber plus coupling agents due to decrease in crystallinity.

References

- (1) S. K. Sharma, A. Tendolkar, and A. Misra, *Molec. Cryst. Liq. Cryst.*, **157**, 597 (1988).
- (2) S. Bhattacharya, K. A. Tendolkar, and A. Misra, *Molec. Cryst. Liq. Cryst.*, **153**, 501 (1987).
- (3) M. Pracella, E. Chiellini, and D. Dainelli, *Macromol. Chem.*, **190**, 175 (1989).
- (4) D. Dutta, H. Fruitwala, A. Kholi, and R. A. Weiss, *Polym. Eng. Sci.*, **30**, 1005 (1990).
- (5) M. Garcia, J. I. Eguiazabal, and J. Nazabal, *Polym. Compos.*, **6**, 686 (2003).
- (6) A. I. Isayev and M. Modic, *Polym. Compos.*, **8**, 158 (1987).
- (7) K. G. Blizard and D. G. Baird, *Polym. Eng. Sci.*, **27**, 653 (1987).
- (8) G. Kiss, *Polym. Eng. Sci.*, **27**, 410 (1987).
- (9) R. A. Weiss, W. Huh, and L. Nicolais, *Polym. Eng. Sci.*, **27**, 864 (1987).
- (10) F. P. La Mantia, A. Valenza, P. L. Magagnini, and M. Paci, *Polym. Eng. Sci.*, **30**, 7 (1990).
- (11) F. P. La Mantia, A. Valenza, and P. L. Magagnini, *J. Appl. Polym. Sci.*, **44**, 1257 (1992).
- (12) S. Rabiej, B. Ostrowska-Gumkowska, and A. Wlochowicz, *Eur. Polym. J.*, **33**, 1031 (1997).
- (13) Y. Seo and K. U. Kim, *Polym. Eng. Sci.*, **38**, 596 (1998).
- (14) E. Shivakumar, K. N. Pandey, S. Alam, G. N. Mathur, and C. K. Das, *Macromol. Res.*, **13**, 81 (2005).
- (15) H. J. Sang and S. K. Bong, *Polym. Eng. Sci.*, **35**, 6 (1995).
- (16) J. W. Lee, S. H. Joo, and J. I. Jin, *Macromol. Res.*, **12**, 195 (2004).