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Blends of Silicone Rubber and Liquid Crystalline Polymer

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Abstract: Blends of silicone rubber (VMQ) and liquid crystalline polymer (LCP) were prepared by the melt mixing technique. Mechanical, XRD, thermal and dynamic mechanical investigations are reported for the pure silicone rubber and blends. The mechanical properties, viz. the tensile strength, tear strength and elongation at break, of the silicone rubber decreased with the addition of LCP. The SEM study on the tensile fractured surface of the blends revealed that they had a two phase structure, and that the failure was mainly due to fiber pull out, which suggests that the VMQ and LCP are incompatible in all of the proportions examined in this study. However, the FTIR study shows that there was a partial interaction between the VMQ and LCP, but which may not be sufficient to grip the fibrils under the applied load. In the XRD analysis, it was observed that the crystalline structure of the silicone rubber deteriorated in the presence of LCP. The DMA study suggested that the storage modulus of the silicone rubber was improved with the addition of LCP, due to the high modulus of the LCP phase. The thermal stability of the silicone rubber was greatly reduced by the addition of LCP, due to the latter having a thermal stability lower than that of silicone rubber.

Keywords: silicone rubber, liquid crystalline polymer, blend, X-ray diffraction (XRD), dynamic mechanical analysis (DMA), crystallinity.

Introduction

Thermotropic liquid crystal polymers (LCP's) are a special class of engineering thermoplastics, which form a highly ordered structure in molten states.[1] Their rigid rod-like molecular conformation and the stiffness of the backbone chains impart a high degree of orientation during melt processing and forms fibrous structures in the final product. They are very easy to process and possess outstanding mechanical properties and high chemical resistance. However, they show high degree of anisotropy in properties,[2] which may be overcome by blending with flexible polymers.[3] Liquid crystalline polymers have also shown that they can impart fibre reinforcement when melt blended with flexible polymers.[4-7] Recent studies have described formation of fibre-like LCP domains in blends processed by conventional techniques, such as extrusion, injection, molding, and fibre spinning.[8-10] Brief reviews on studies of blends of isotropic polymers and thermotropic liquid crystalline polymers are given by Brostow,[11] by Isayev and Limtasiri,[12] and Dutta *et al.*[13] Since the LCP forms the fibres in the melt state, there is considerably lower wear and tear on the processing machinery in comparison to conventional reinforcing glass fibres. There is also a viscosity reduction reported in the above studies, which imparts better flow properties to

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the blends. The mechanical properties of blends are significantly affected by the mode of dispersion, the shape, and orientation of LCP and interfacial adhesion between two phases.[14-16]

In the present paper we investigated the thermal, XRD and dynamic mechanical properties of silicone rubber and thermotropic liquid crystalline polymer blend and correlated with their technical properties.

Experimental

The chemical structure of the raw materials used in this study is shown in Table I. Silicone rubber (VMQ) used was Silastic NPC-40 from Dow Corning (USA), Thermotropic liquid crystalline polymer (TLCP) was Vectra A 950 from Hoechst Celanese (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 mixing formulation is shown in Table II. The mixing of LCP with silicone rubber was done with the help of high temperature sigma internal mixer at 290 °C for 8 min. 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 thus prepared.

Fourier transform infrared spectroscopy (FTIR) experiments were done on uncured samples of VMQ, LCP, and their blends using a NEXUS 870 FTIR (Thermo Nicolet) in humidity less atmosphere at room temperature. A total of 32 scans were averaged with a resolution of 4 cm^{-1}. The cure characteristics of the blends were studied using a Monsanto rheometer (R-100) at 170 °C. Tensile properties of the blends were tested on a HOUNSFIELD (model H10KS) universal testing machine at a test speed of 500 mm/min. Dynamic fracture mechanism of the blends were studied by Scanning Electron Microscope (SEM)(JSM-5800 of JEOL Co.), after auto sputter coating of the fractured surface with gold at 0° tilt angle. X-ray diffraction was performed with PW 1840 X-ray Diffractometer with copper target ($Cu\text{-}K_\alpha$) at a scanning rate of 0.05° 2θ/sec, chart speed 10 mm/2θ, range 5,000 c/s, and a slit of 0.2 mm, applying 40 kV, 20 mA, to asses the change of crystallinity of the blends as a function of blend ratio.[17,18] 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 μm at a frequency of 1 Hz from 25 to 250 °C and a heating rate of 5 °C/min. Thermo gravimetric analysis (TGA) was carried out using TGA-2100 DuPont instrument in presence of nitrogen from 25- 680 °C, with a heating rate of 10 °C/min.

Table II. Sample Codes and Compounding Formulations*

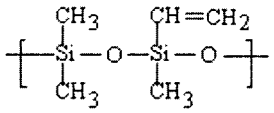
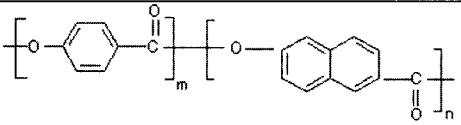
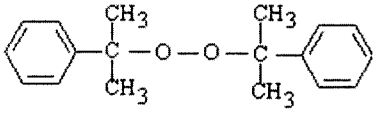
Sample No.	A	B	C	D
VMQ	100	90	80	60
LCP	0	10	20	40

*All blends contain 1 phr Varox DCP 40 C with respect to rubber content.

Results and Discussion

In order to study the interaction between silicone rubber and LCP, the IR study has been conducted. The IR spectra of the molded thin film of VMQ and the blends with the composition of 10 and 20 weight percent LCP are shown in Figure 1. Figure 1(a) and 1(b) shows the characteristic bands of VMQ and the blends, respectively. The assignment of various peaks for the pure silicone rubber and LCP are given in Table III. These bands, assigned here, are in good agreement with the literature values.[19] Out of all characteristic bands for various groups in the blend, the following

Table I. Molecular Structure of Raw Materials

Material (Code)	Commercial Name	Molecular Structure	M_w (kg/mol)
Silicone Rubber (VMQ)	Silastic NPC40C		> 500
Liquid Crystalline Polymer (LCP)	Vectra A 950		> 20
Dicumyl Peroxide (DCP)	Varox 40 C		-

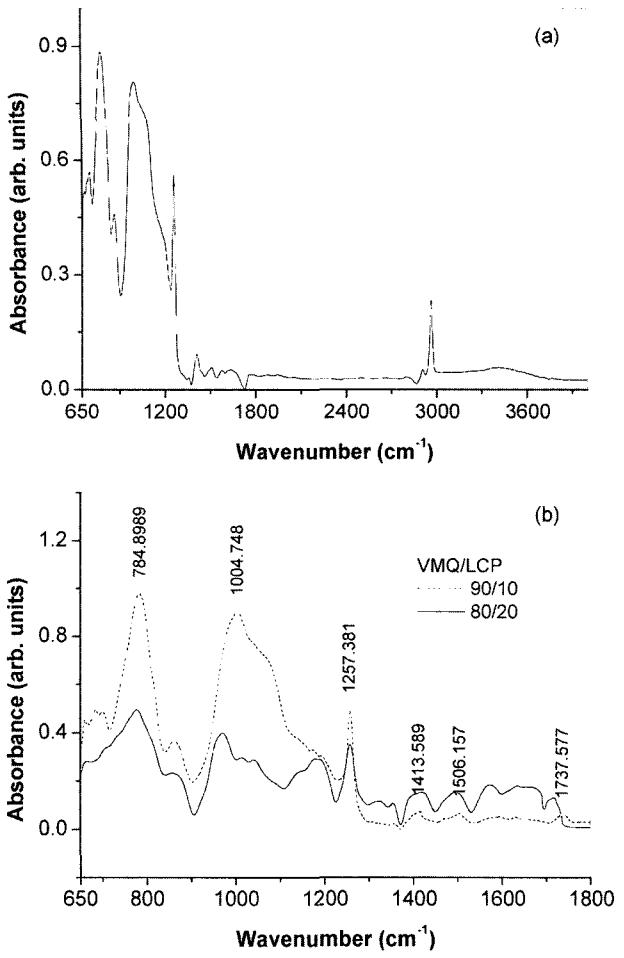


Figure 1. IR spectra of molded thin film of (a) pure silicone rubber and (b) blends of VMQ/LCP with the composition of 90/10 and 80/20.

Table III. Assignment of IR Bands of (a) Silicone Rubber and (b) Liquid Crystalline Polymer

Wavenumber (cm^{-1})	Assignment
(a) Silicone rubber	
783, 865	Si-CH_3 stretching
1257	Si-CH_3 rocking
1409, 1500-1600	Si-CH=CH_2
1000	Si-O-Si asym. stretching
2962	C-H stretching
(b) Liquid crystalline polymer	
1733	C=O stretching
1149	C-O-C sym. stretching
1257	C-O-C asym. stretching
1400-1600	C=C stretching
3075	C-H stretching

peaks are clearly identified: 784, 865, and 1257 cm^{-1} of Si-CH_3; 1400-1600 cm^{-1} either of Si-CH=CH_2 of VMQ or C=C of LCP; 1004 cm^{-1} of Si-O-Si; 1737 cm^{-1} of C=O. The IR spectra of 10 wt% LCP blend resembles to that of pure silicone rubber. The Si-CH=CH_2 band of pure silicone rubber at 1409 cm^{-1} and the C=O peak of pure LCP at 1733 cm^{-1} are slightly shifted to higher frequency side in the VMQ/LCP 90/10 blend. However, the Si-CH_3 peaks remain unchanged in their positions. At higher level of LCP, the peaks in the range of 1400-1600 cm^{-1} of VMQ appeared to be broader and C=O peak of LCP shifted nearly 14 cm^{-1} to lower frequency side, this suggest that there is a considerable interaction between C=O of LCP and Si-CH=CH_2 of VMQ. However, the C=C peaks of LCP and Si-CH=CH_2 of VMQ falls in the same region, hence it is difficult to substantiate the above interpretation. If there is any interaction at Si-CH=CH_2 environment, it must produce some change in Si-O-Si asymmetric stretching, due to its chemical structure (Table I). As it is expected, the Si-O-Si peak of silicone rubber at 1000 cm^{-1} is split in to two main peaks in presence of LCP. The new peak at 1178 cm^{-1} owing to be different chemical environment of Si-O-Si. This confirms that there is a significant interaction between Si-CH=CH_2 of VMQ and C=O of LCP.

The cure characteristics of the samples were studied at 170 °C and shown in Figure 2. The processing parameters and the other technical properties are given in Table IV. The maximum state of cure (τ_{max} - τ_{min}) was observed for the blend containing 20 wt% LCP, followed by pure silicone rubber, 10 wt% and 40 wt% LCP blends. The swelling coefficient values in organic solvent confirm the above findings. From the rheograph it is observed that the minimum viscosity (i.e., τ_{min}) of the elastomer decreases with the addition of 10 wt% LCP, and further gradual increment is observed with the higher loading of LCP in the blend. This seems to indicate that; the LCP acts as a lubricating agent

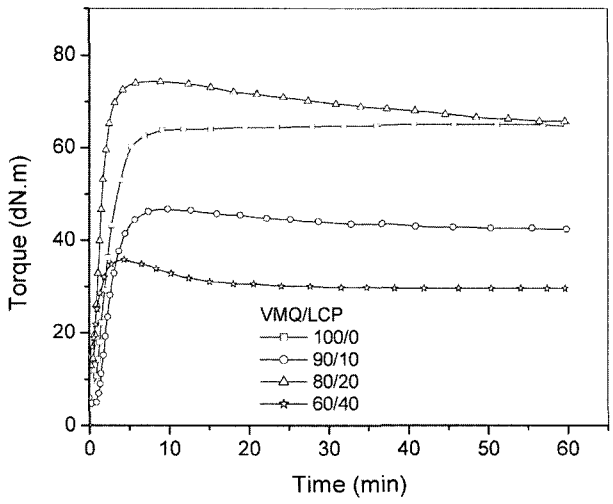


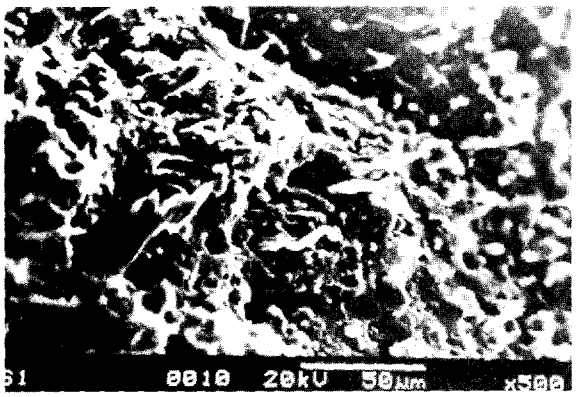
Figure 2. Rheograph of the silicone rubber and blends.

Table IV. Technical Properties

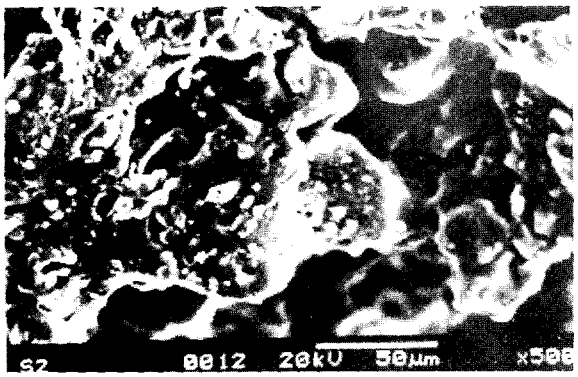
Sample No.	A	B	C	D
Tensile Strength (MPa)	4.79	1.96	2.57	3.24
Elongation at Break (%)	540	140	90	75
Tear Strength (N/mm)	13.70	9.93	11.11	12.82
τ_{max} - τ_{min} (dN.m)	54	42	61	20
τ_{min} (dN.m)	10	5	13	16
Swelling Coefficient	1.2	1.3	0.9	1.2

for silicone rubber at its lower level. However, the rate of cure slowly increased with the increment of LCP, which suggest that the LCP accelerate the vulcanization reaction of the elastomer.

The tensile properties of the elastomer found to decrease by blending with the LCP. The elongation at break (E.B.) drastically reduced with the increasing LCP content. The maximum E.B. 540% is observed for the pure polymer, whereas for the 40 wt% LCP the E.B. is 75% only. This means that the addition of LCP made the matrix stiffer and more brittle; hence we could not see even 100% elongation for the blends with the composition of 20 and 40 wt% LCP.



(a)



(b)

Figure 3. SEM micrographs of blends VMQ/LCP (a) 90/10 and (b) 80/20.

Such behaviour is a characteristic of all fibre-reinforced composites. The tensile strength and tear strength value of the elastomer sharply decreased with the addition of 10 wt% LCP, and further slowly rises with increase in the LCP content. This reduction in the tensile strength value is due to lack of interfacial adhesion between LCP and elastomer as shown in Figure 3(a) and 3(b). Figure 3(a) is a micrograph of a tensile fractured surface of a 10 wt% LCP blend, shows the fibrous nature of the domains of the LCP. The blend containing 20 wt% LCP showed lower fibrillar morphology than the 10 wt% LCP blend and it showed non-uniform distribution of LCP fibrils in the matrix phase, whereas in 10 wt% LCP blend sharp elongated fibrils uniformly distributed in the matrix. This may be the reason for decrease in the viscosity for the later system because of the formation of elongated fibrils of the LCP phase, which tends to lubricate the melt.[20] In both the cases holes were observed on the surface of the samples due to pull out of the fibrils from the matrix phase during fracture, which indicates poor adhesion between two phases.

The X-ray diffractograms of the blends has been shown in Figure 4. The diffractogram shows one broad peak and two clear sharp peaks at 2θ= 15°, 22° and 38° respectively. The peaks at 2θ=22° and 38° of silicone rubber are slowly enhanced in intensity with the increment of LCP, however,

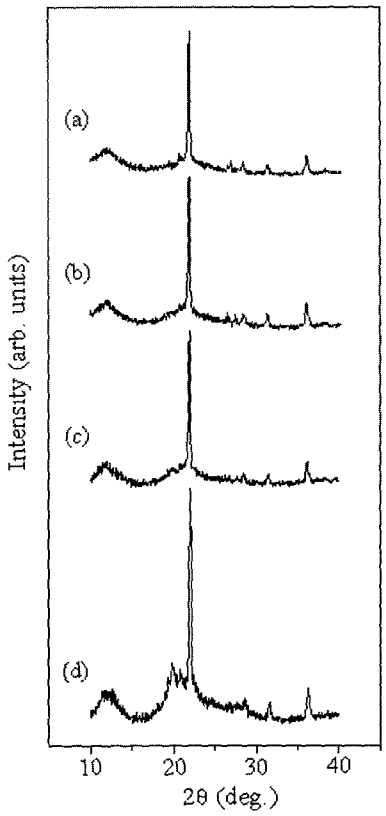


Figure 4. X-ray diffractograms of the VMQ/LCP blends (a) 100/0, (b) 90/10, (c) 80/20, and (d) 60/40.

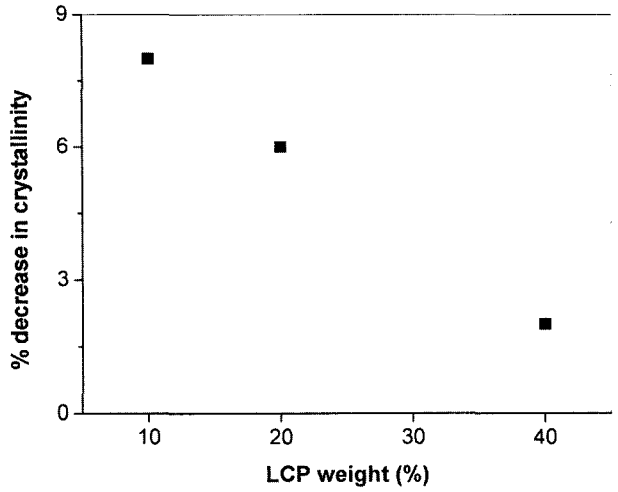


Figure 5. Percent decrease in thecrystallinity of VMQ as a function of LCP weight percentage.

the amorphous peak at $2\theta=15°$ has become broader and more intense with the higher loading of LCP in the silicone matrix. It is interesting to note that the intense peak[21] of LCP at $2\theta=19.9°$ was not observed for the blends up to 20 wt% LCP. Whereas, for the blend with 40 wt% LCP, a broad peak with low intensity was observed, which is partially overlapped with the high intense peak ($2\theta=22°$) of silicone rubber. The degree of crystallinity of the blends has been calculated by using I_c/I_a+I_c equation[17,18] where, I_c and I_a are integrated intensities of crystalline and amorphous phases, respectively. Figure 5 shows the percent decrease in the crystallinity of VMQ with the increment of LCP. Addition of 10 wt% LCP the blend showed nearly 8% lower crystallinity than the pure silicone rubber and further slight increase in the crystallinity was observed with the higher loading of LCP. However, all the blends showed lower crystallinity than the pure silicone rubber. This suggests that the LCP disrupts the crystalline ordered structure of silicone rubber.

The storage modulus (E'), loss tangent (tan δ) and loss modulus (E'') of the blends as a function of temperature has been shown in Figure 6(a)-6(c). From the Figure 6(a) it is found that the storage modulus of the silicone rubber slightly enhanced with the addition of 10 wt% LCP, further dramatic increase in E' was observed with the higher loading of LCP. This improvement in E' is due to the high modulus of LCP phase, which consists of rigid rod like molecules. As it is observed 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 2-5 times higher than the pure elastomer throughout the temperature range studied. The loss tangent (tan δ) as a function of temperature has been shown in Figure 6(b). The tan δ values of the blends much higher than the pure rubber, this

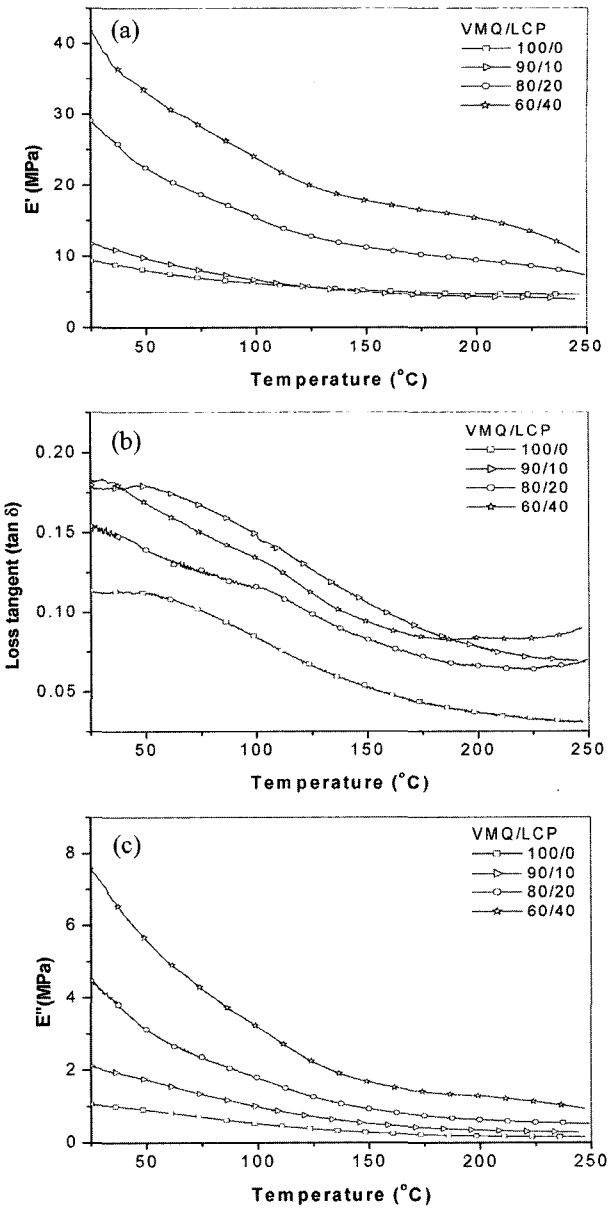


Figure 6. (a) storage modulus ,(b) loss tangent, and (c) loss modulus of the samples as a function of temperature.

may be due to lower crystallinity of the blends in comparison with the pure silicone rubber.[22] From the Figure 6(c) it has been observed that the loss modulus of the elastomer largely increases with the addition of LCP. This further confirms that the interfacial adhesion between two polymers is poor; hence much energy must have dissipated at the polymer fibre interfaces or at fibre end.[23]

Thermogravimetry (TG) and differential thermogravimetry (DTG) curves for the blends are shown in Figure 7(a) and 7(b) and the corresponding thermal parameters are given in Table V. The peak height in Figure 7(b) show higher rate of degradation for the LCP than the silicone rub-

Table V. TGA/DTG Parameters

Sample No.	Onset Deg. Temp. (°C)	Loss of Weight (%)	DTG Peak Temp. (T_{max}) (°C)	dW/dt (%/min)
A	451	55	536	5.9
C	434	54	503	11.9
D	441	61	506	12.6
LCP	484	54	510	15.8

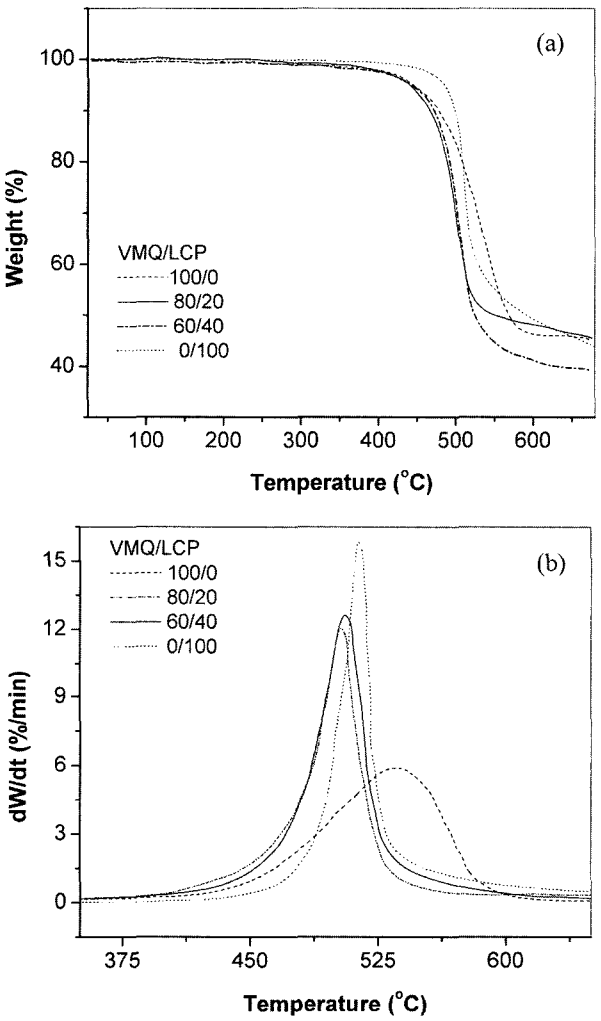


Figure 7. (a) thermograms and (b) differential thermograms of the samples.

ber. 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. For the pure silicone rubber the degradation started at 451 °C continued up to 590 °C, where as for the blends the degradation has occurred with in the temperature range of 431-550 °C. And also from the Figure 7(b), it has been observed that the temperature, where the maximum rate of degradation occurs, (T_{max}) of the elastomer rapidly decreased with the addition of 10 wt% LCP, and further slight increase in T_{max} was observed. It appeared that the incorporation of LCP destabilizes the silicone rubber to some extent. This phenomenon could indeed be due to the influence of the degraded products of LCP, which may react with silicone rubber under these conditions, and imply a possible modification in the degradation mechanism of elastomer. The rate of degradation at T_{max} (dW/dt) is found to increase with the increase of LCP content in the blend, which suggests that the LCP accelerates the degradation process of silicone rubber.

Conclusions

The mechanical, XRD, and thermal properties of blends of silicone rubber with LCP were investigated. Significant decrease in the blend viscosity was observed at the lower level of LCP. FTIR study revealed partial interaction between VMQ and LCP, however, this interaction may not be sufficient to grip the LCP fibrils under the applied load hence, lower mechanical properties were observed for all the blends, which is further confirmed by the SEM study. From the XRD study it has been observed that the crystalline structure of the silicone rubber deteriorates with the addition of LCP. The storage modulus, loss modulus and loss tangent were much higher for the blends in comparison with the silicone rubber. The high modulus for the blends is due to the LCP phase, which consists of rigid rod-like molecules. Thermal stability of the elastomer found to decrease with the addition of LCP due to lower thermal stability of LCP compared to silicone rubber.

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