

**STUDIES ON PC/SEBS AND SEBS-g-MA BLENDS
AND PC/SEBS-g-MA/WOLLASTONITE
COMPOSITES**

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AND PC/SEBS-g-MA/WOLLASTONITE
COMPOSITES**

by

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Submitted

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to the



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Dedicated To
My Family

CERTIFICATE

This is to certify that the thesis entitled “**Studies on PC/SEBS and SEBS-g-MA Blends and PC/SEBS-g-MA/Wollastonite Composites**” being submitted by **Ms. Astha Garhwal**, to the Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy** in the Centre for Polymer Science and Engineering, is a record of bonafide research work carried out by her. Astha Garhwal has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this thesis have not been submitted, in part or full, to any other university or Institute for the award of any degree or diploma.

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Abstract

The goal of this research is to develop polycarbonate (PC)/styrene-ethylene-butylene-styrene (PC/SEBS) and PC/styrene-ethylene-butylene-styrene grafted maleic anhydride (PC/SEBS-g-MA) blends and the latter's wollastonite reinforced composites and investigate the effects of SEBS, SEBS-g-MA and wollastonite on thermal, mechanical, thermo – mechanical, fracture, morphological and viscoelastic behavior. In this work binary blends of PC/SEBS and PC/SEBS-g-MA at varying concentrations (5 to 50 phr) of SEBS and SEBS-g-MA were prepared by first dry blending followed by melt mixing. The blend composition with 35 phr of SEBS-g-MA was optimized for composite preparation in terms of best combination of stiffness and toughness properties. PC/SEBS-g-MA/wollastonite composites were prepared by varying concentrations (5 to 50 phr) of wollastonite.

For PC/SEBS blends a decrease in tensile modulus and strength was observed where tensile strength decreased by 12 to 80 % while tensile modulus decreased by 20 to 76 % at the volume fraction (Φ_d) = 0.06 – 0.40 of SEBS. Notched Izod impact strength was enhanced significantly in presence of SEBS and the blends became non-breakable at Φ_d = 0.21–0.40. The dependence of impact strength on the blending elastomer concentration and interparticle distance of the dispersed phase were analysed. The fracture properties were studied by essential work of fracture method. It is revealed that non-essential or plastic work increased with an increased amount of SEBS. In DMA the storage modulus and the loss modulus values for the blends decreased with increase in SEBS content and the values lie in between the modulus values of neat PC and SEBS. The $\tan \delta$ values were obtained experimentally and compared with a predictive model. Melt rheological properties of PC/SEBS blends are studied using capillary rheometer at shear rate range from 10^2 s^{-1} to 10^4 s^{-1} and at 270 °C, 280 °C and 290 °C. With increase in SEBS content melt viscosity decreased which may be due to the plasticization introduced by the presence of elastomer along with the low viscosity of the dispersed phase. In dynamic rheological analysis PC showed a nearly Newtonian behavior while shear thinning behavior is shown by the blends indicating an ease in processibility of the blends.

For PC/SEBS-g-MA blends a significant enhancement in notched Izod impact strength is observed and blends become unbreakable at Φ_d = 0.21-0.39 while tensile modulus and strength decreased by 6 to 69 % and 9 to 56 %, respectively at Φ_d = 0.06 - 0.39. Interparticle distance of the dispersed phase evaluated from the morphology studies by scanning electron microscopy (SEM) and the impact strength dependence on the concentration of the blending rubber are analysed. With increasing SEBS-g-MA concentration nonessential or plastic work increases which explains the enhancement of impact strength of the blends. In DMA decrease in both the storage and loss modulus values are observed with increasing SEBS-g-MA content in the blends. With increase in SEBS-g-MA content melt viscosity decreased due to the plasticization introduced by the presence of elastomer and also due to the low viscosity of the dispersed phase. PC/SEBS-g-MA blends followed power law relationship during melt flow. Increase in shear stress is observed with shear rate, however the shear stress decreased with increase in SEBS-g-MA content at all the temperatures. Lower value of activation energy in the blends than that of neat PC indicated that addition of SEBS-g-MA eases the flow. In dynamic rheological analysis The blends demonstrated liquid like behaviors along with decreased $\tan \delta$ values.

The increased tensile modulus on addition of wollastonite in PC/SEBS-g-MA blend indicated that wollastonite was effective in increasing stiffness. In the presence of wollastonite, Izod

impact strength of PC/SEBS-g-MA blends decreased, however it was still higher than that of neat PC up to 35 phr of wollastonite. The DMA study revealed increase in both the storage and loss modulus which are attributed to homogeneous dispersion of rigid wollastonite and reinforcement effect of the filler which restricted the mobility of the blend in the composites. The T_g of the composites increased indicating some extent of phase interaction between the matrix and filler. Shear thinning behaviour was shown by PC/SEBS-g-MA/wollastonite composites. The values of melt viscosities increased with wollastonite content which may be due to the restriction in flow of the blend polymer chains by wollastonite. Increase in shear stress was observed with shear rate, and with increase in wollastonite content at all the temperatures. Higher value of activation energy in the composites than that of the matrix blend indicated that addition of wollastonite restricts the flow. In dynamic rheological analysis monotonous increase in storage and loss modulus on incorporation of wollastonite was observed. The enhanced properties indicate some phase interaction between the filler and blend matrix. In the PC/SEBS-g-MA/wollastonite composites shear thinning behavior was observed which contributes significantly in power savings during processing. The dynamic rheological properties of PC/SEBS-g-MA/wollastonite composites exhibited a possibility of improving processibility of PC by the incorporation of wollastonite.

सार

इस शोध का लक्ष्य पॉली कार्बोनेट (पीसी) / स्टायरन-एथिलीन-ब्यूटीलीन-स्टायरिन विकसित करना है (पीसी / एसईबीएस) और पीसी / स्टेरिन-एथिलीन-बीथिलीन-स्टैरीन कम्बल मेनिक एनहाइडाइड (पीसी / एसईबीएस-जी-एमए) मिश्रणों और उत्तरार्द्ध की वोलस्टोनेइट प्रबलित कंपोजिट्स और थर्मल पर एसईबीएस, एसईबीएस-जी-एमए और वॉल्साटोनाइट के प्रभावों की जांच, यांत्रिक, थर्मामीटरों - यांत्रिक, फ्रैक्चर, आकृति विज्ञान और विस्कोलैस्टिक व्यवहार। इस काम में एसईबीएस और एसईबीएस-जी-एमए के सांद्रता (5 से 50 एफआर) में पीसी / एसईबीएस और पीसी / एसईबीएस-जी-एमए की द्विआधारी मिश्रणों को पिघल मिश्रण के बाद पहले शुष्क मिश्रण से तैयार किया गया था। एसईबीएस-जी-एमए के 35 फ्रे के साथ मिश्रण संयोजन कठोरता और क्रूरता गुणों के सर्वोत्तम संयोजन के संदर्भ में समग्र तैयारी के लिए अनुकूलित किया गया था। पीसी / एसईबीएस-जी-एमए / विलोस्टोनिट कम्पोजिट्स को वोलस्टोनेट के सांद्रता (5 से 50 एफआर) के अलग-अलग करके तैयार किया गया था। पीसी / एसईबीएस के लिए तन्यता मापांक में कमी आती है और ताकत को देखा जा सकता है जहां तन्य शक्ति 12 से 80% कम हो जाती है, जबकि तन्यता मापांक मात्रा अंश (Φ_d) = 0.06- 0.40 सेबीस में 20% से 76% की कमी आई है। एसईबीएस की मौजूदगी में नोबेल आईजोड प्रभाव शक्ति को काफी बढ़ाया गया और यह मिश्रण $\Phi_d = 0.21-0.40$ पर गैर-भंगुर हो गया। सम्मिश्रण इलास्टोमेर एकाग्रता और फैलाने वाले चरण की अंतःक्रिया दूरी पर प्रभाव शक्ति की निर्भरता का विश्लेषण किया गया। अस्थिभंग के गुणों को फ्रैक्चर विधि के महत्वपूर्ण काम से अध्ययन किया गया था। यह पता चला है कि एसईबीएस की बढ़ी हुई मात्रा के साथ गैर आवश्यक या प्लास्टिक का काम बढ़ गया है। डीएमए में भंडारण मापांक और मिश्रण के लिए हानि मापांक मूल्य एसईबीएस सामग्री में वृद्धि के साथ घट गए हैं और मूल्य सुस्त पीसी और एसईबीएस के मापांक मूल्यों के बीच में है। तन δ मान प्रयोगात्मक रूप से प्राप्त किए गए थे और एक पूर्वानुमान मॉडल के साथ तुलना में। पीसी / एसईबीएस मिश्रणों के रियोलॉजिकल गुणों को 10 से 102 एस -1 के बीच कतरनी दर सीमा पर केशिका रेमोमीटर के माध्यम से और 270 डिग्री सेल्सियस, 280 डिग्री सेल्सियस और 29 डिग्री सेल्सियस पर अध्ययन किया जा रहा है। एसईबीएस सामग्री में वृद्धि के साथ चिपचिपाहट कम हो जाती है, जो फैलाने वाले चरण की कम चिपचिपाहट के साथ इलास्टोमेर की उपस्थिति द्वारा शुरू की गई प्लास्टिक के कारण हो सकती है। गतिशील rheological विश्लेषण में पीसी लगभग न्यूटनियन व्यवहार दिखाता है, जबकि कतरनी पतला व्यवहार मिश्रणों द्वारा दिखाया जाता है जो मिश्रणों की संसाधितता में आसानी का संकेत देता है। पीसी / एसईबीएस-जी-एमए के लिए इजोड के प्रभाव की ताकत में उल्लेखनीय वृद्धि देखी जाती है और $\Phi_d = 0.21-0.39$ पर मिश्रणों को अबाधित किया जाता है, जबकि तन्य मापांक और ताकत क्रमशः 6 से 69% और 9 से 56% की दर से घट जाती है जबकि $\Phi_d = 0.06 - 0.39$ इलेक्ट्रॉन माइक्रोस्कोपी (एसईएम) को स्कैन करके आकृति विज्ञान के अध्ययनों से मूल्यांकन किए गए फैलाने वाले चरण की इंटरफार्टिकल दूरी और मिश्रण रबर की एकाग्रता पर प्रभाव शक्ति निर्भरता का विश्लेषण किया जाता है। बढ़ते एसईबीएस-जी-एमए एकाग्रता के साथ गैर-प्रासंगिक या प्लास्टिक का काम बढ़ता है जो मिश्रणों के प्रभाव की ताकत बढ़ाने की व्याख्या करता है। दोनों भंडारण और हानि मापांक मूल्यों में डीएमए कमी में मिश्रणों में बढ़ते SEBS-g-MA सामग्री के साथ मनाया जाता है। एसईबीएस-जी-एमए सामग्री में वृद्धि के साथ इलास्टोमेर की उपस्थिति द्वारा शुरू की गई प्लास्टिकाई के कारण चिपचिपापन कम हो गया और फैलाने वाले चरण की कम चिपचिपाहट के कारण। पिघल प्रवाह के दौरान पीसी / एसईबीएस-जी-एमए मिश्रणों के बाद बिजली कानून संबंधों का पालन करता है कतरनी दर के साथ कतरनी तनाव में वृद्धि देखी जाती है, हालांकि सभी तापमान पर SEBS-g-MA सामग्री में वृद्धि के साथ

कतरनी तनाव में कमी आई है। साफ पीसी की तुलना में मिश्रणों में सक्रियण ऊर्जा के कम मूल्य से संकेत मिलता है कि एसईबीएस-जी-एमए के बढ़ने से प्रवाह कम हो जाता है। डायनेमिक रियोलॉजिकल विश्लेषण में मिश्रणों ने तरल जैसे व्यवहार की कमी हुई तन δ मूल्यों को दर्शाया।

पीसी / एसईबीएस-जी-एमए मिश्रण में वोल्स्टोनाइट के अलावा बढ़े हुए तन्यता मापांक ने संकेत दिया कि कठोरता में वृद्धि के लिए वोल्स्टोनाइट प्रभावी था Wollastonite की उपस्थिति में, पीसीओ / एसईबीएस-जी-एमए मिश्रणों की इज़ोड प्रभाव शक्ति में कमी आई है, हालांकि यह साफ पीसी के मुकाबले अभी भी 35 वें Wollastonite की तुलना में अधिक है। डीएमए अध्ययन से पता चला है कि भंडारण और हानि के दोनों मॉड्यूलस में वृद्धि हुई है जो कठोर वोल्स्टोनाइट के समसामयिक फैलाव और भराव के सुदृढीकरण प्रभाव के लिए जिम्मेदार हैं, जो कि कंपोजिट में मिश्रण की गतिशीलता को प्रतिबंधित करती है। कंपोजिट के टीजी मैट्रिक्स और भराव के बीच कुछ हद तक चरण बातचीत का संकेत देते हुए बढ़े। पीसीआर / एसईबीएस-जी-एमए / वोल्स्टोनट कंपोजिट्स द्वारा दिखाया गया शियर पतला व्यवहार पिघला हुआ चिपचिपाहट के मूल्यों में वोल्स्टोनाइट सामग्री के साथ बढ़ोतरी हो सकती है जो वाल्स्टोनाइट द्वारा मिश्रित बहुलक श्रृंखलाओं के प्रवाह में प्रतिबंध के कारण हो सकती है। कतरनी दर में वृद्धि, कतरनी दर के साथ मनाई गई थी, और सभी तापमानों पर wollastonite सामग्री में वृद्धि के साथ। मैट्रिक्स मिश्रण की तुलना में कंपोजिट में सक्रियण ऊर्जा के उच्च मूल्य में संकेत दिया गया है कि वोल्स्टोनाइट के अतिरिक्त प्रवाह को नियंत्रित करते हैं गतिशील rheological विश्लेषण में wollastonite के समावेश पर भंडारण और हानि मापांक में नीरस वृद्धि देखी गई थी। एन्हांस्ड प्रॉपर्टी से भराव और मिश्रण मैट्रिक्स के बीच कुछ चरण की बातचीत का संकेत मिलता है। PC / SEBS-g-MA / Wollastonite कम्पोजिट में कतरनी पतली व्यवहार देखा गया था जो प्रसंस्करण के दौरान बिजली बचत में महत्वपूर्ण योगदान देता है। पीसी / एसईबीएस-जी-एमए / विलोस्टोनिट कम्पोजिट्स के डायनेमिक रियोलॉजिकल गुणों ने वोल्स्टोनाइट को शामिल करके पीसी की प्रोसेसिबिलिटी में सुधार की संभावना का प्रदर्शन किया।

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List of abbreviations and symbols

ABS	- Poly(acrylonitrile-co-butadiene-co-styrene)
ABS-g-MA	- Maleic anhydride functionalized acrylonitrile-butadiene-styrene
ASTM	- American Society for Testing and Materials
CaCO ₃	- Calcium carbonate
CaSiO ₃	- Calcium silicate
COPE	- Copolyether ester elastomer
CTOD	- Crack-tip opening displacement
DENT	- Double-edge-notched-tension
DMA	- Dynamic mechanical analysis
DSC	- Differential scanning calorimeter
D _n	- Number average domain size
D _w	- Weight average domain size
D _v	- Volume average domain size
EPDM	- Ethylene propylene diene monomer rubber
EPDM-g-MA	- Ethylene propylene diene grafted maleic anhydride
eEPDM	- Epoxidized EPDM
<i>E</i>	- Tensile modulus
<i>E'</i>	- Storage modulus
<i>E''</i>	- Loss modulus
EWF	- Essential work of fracture
FPZ	- Frontal process zones
<i>G'</i>	- Melt storage modulus/Elastic modulus
<i>G''</i>	- Melt loss modulus/Viscous modulus

HDPE	-	High density polyethylene
ID	-	Interparticle distance
IFPZ	-	Inner fracture process zone
J_c	-	Critical J -integral value
MFI	-	Melt flow index
MMT	-	Montmorillonite
PA	-	Polyamide
PC	-	Polycarbonate
PS	-	Polystyrene
SBS	-	Styrene-butadiene –styrene block copolymer
SEBS	-	Styrene – ethylene – butylenes – styrene block copolymer
SEBS-g-MA	-	Styrene – ethylene – butylenes – styrene grafted with maleic anhydride
SEM	-	Scanning electron microscopy
SIS	-	Styrene – isoprene – styrene block copolymer
SMA	-	Styrene - maleic – anhydride copolymer
TGA	-	Thermogravimetric analysis
TPE	-	Thermoplastic elastomer
T_g	-	Glass transition temperature
ΔE	-	Activation energy
Φ_d	-	Volume fraction of the dispersed phase
Φ_f	-	Volume fraction of the filler
τ	-	Matrix ligament thickness
τ_w	-	Shear stress
η^*	-	Complex Viscosity
